materials proceedings

MDPI

Proceeding Paper

The Influence of the Quality of Brick Firing on Their Calcium Diffusion Capacity and Biodegradation Potential—A Preliminary Study †

Klára Kobetičová [1,*], Jana Nábělková [1], Martin Keppert [1], Igor Medveď [2], Zbigniew Suchorab [1,3] and Robert Černý [1]

[1] Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 16629 Prague, Czech Republic
[2] Faculty of Civil Engineering, Slovak University of Technology, Radlinského 11, 810 05 Bratislava, Slovakia
[3] Faculty of Environmental Engineering, Lublin University of Technology, Nadbystrzycka 40B, 20-618 Lublin, Poland
* Correspondence: klara.kobeticova@fsv.cvut.cz
† Presented at the 10th MATBUD'2023 Scientific-Technical Conference "Building Materials Engineering and Innovative Sustainable Materials", Cracow, Poland, 19–21 April 2023.

Abstract: The diffusion of calcium ions Ca^{2+} in aquatic solutions (10 g/l) was measured for two brick samples from a region in Bohemia (Vysoké Mýto, Holešov-Žopy). The experiment was performed under laboratory conditions at the ambient temperature of 20 ± 2 °C for a period of 240 h. The bricks were cut into three depth layers. The calcium concentrations were analyzed chelatometrically. The biodegradation potential of the individual layers was also studied. The results indicated that the depth and quality of firing are of importance regarding the transport of calcium, and they affect the success of bio-colonization.

Keywords: calcium; diffusion; brick; biodegradation; biofilm; porosity

Citation: Kobetičová, K.; Nábělková, J.; Keppert, M.; Medveď, I.; Suchorab, Z.; Černý, R. The Influence of the Quality of Brick Firing on Their Calcium Diffusion Capacity and Biodegradation Potential—A Preliminary Study. *Mater. Proc.* **2023**, *13*, 6. https://doi.org/10.3390/materproc2023013006

Academic Editors: Katarzyna Mróz, Tomasz Tracz, Tomasz Zdeb and Izabela Hager

Published: 13 February 2023

1. Introduction

Fired bricks have been used by people since 5000 BC in Mesopotamia and many types of this building material are still produced. Many historic buildings are built from classic, load-bearing, non-perforated and non-relieved bricks, which can be expected to be subjected to relatively large diffusion processes or easier biodegradation than lightweight perforated bricks. It can be assumed that the quality of brick firing is of great importance. The middle part of fired bricks may contain a black or grey reduction core, which distinguishes it from the red color of the rim or surface of the fired clay body. Such a black core can be found in many commercial bricks [1], its presence indicating insufficient firing and incomplete burn-out of organic components present in the used clay.

Diffusion plays a fundamental role in the distribution and behavior of substances in porous building materials. This is well described, especially for Cl^- anions [2–5]. Cations have not been studied as much from this point of view [6]. The exception is radionuclides, but in this case the research is focused on the disposal of hazardous waste, in which less dangerous model elements [7–9] were used. At the same time, cations also play an important role in salinization of building materials, of which calcium is an example. This element occurs in free or bound form as Ca^{2+}. It is among the elements that are important in the metabolic processes of humans and other organisms. Calcium cations are naturally present in water and soil, but they can also enter the environment excessively during liming of fields [10] and, to a lesser extent, during the salting of roads ($CaCl_2$) as a less dangerous salt for the environment than NaCl or KCl [11]. The Ca^{2+} concentration is easy to assess via complexometric titration [12].

Biodegradation of fired bricks has been described in many studies performed in situ and also under laboratory conditions. The presence of algae, cyanobacteria and fungi [13–15] was studied. Their colonization depends on many factors, such as humidity, the amount of light, nutrients and also the structure of the surface of building materials on which organisms can create and maintain biofilm growth, e.g., Ref. [16]. So far, the influence of the degree of the firing of bricks on their ability to be bio-colonized has never been investigated.

In this work, the focus was placed on the influence of the quality of the firing of bricks from the surface to the depth on: (1) the ability of calcium diffusion; and (2) the effect of the firing on the success of the biological colonization of individual layers.

2. Materials and Methods

The model samples were fired bricks from brickyards situated in the towns of: (a) Vysoké Mýto and (b) Holešov-Žopy (Czech Republic) (Figure 1). Dry brick samples in the shape of discs (d = 5 cm, h = 1 cm) represented three layers from the surface to the depth of the brick (0–1 cm, 1–2 cm and 2–3 cm). The composition of brick samples is described in previous literature [17,18]. Pore size distribution, bulk density, total porosity and the specific surface area, determined by Mercury Intrusion Porosimetry, are described in Figures 2 and 3 and in Table 1.

Figure 1. Cutouts of bricks: Vysoké Mýto (left) and Holešov-Žopy (right).

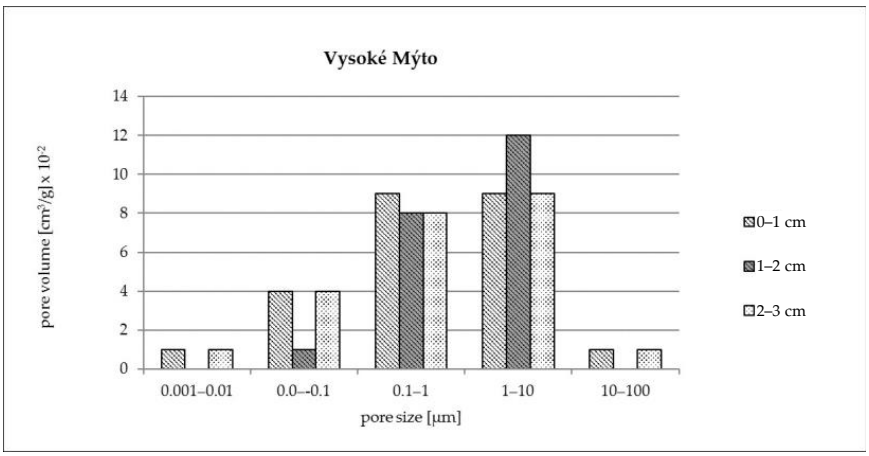

Figure 2. Pore size distribution of individual layer of the brick: Vysoké Mýto (0–1 cm, 1–2 cm, 2–3 cm from the cover).

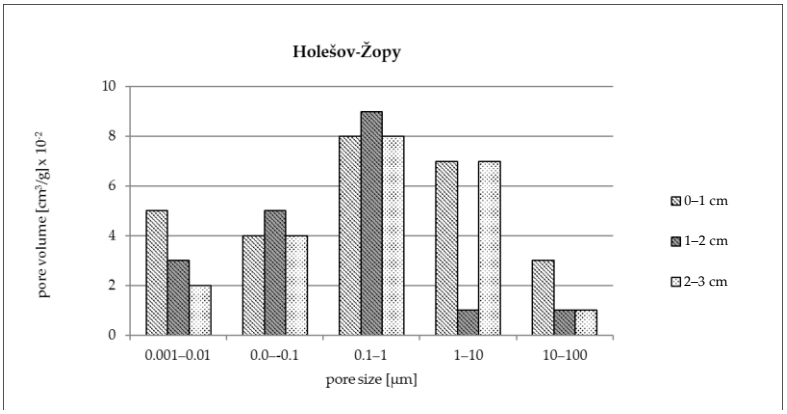

Figure 3. Pore size distribution of individual layer of the brick Holešov-Žopy (0–1 cm, 1–2 cm, 2–3 cm from the cover).

Table 1. Selected properties of the tested bricks—specific surface area (m/g), total cumulative volume (cc/g), total porosity (%) and bulk density (g/cm^3). The mean values from three replicates are used in the table.

Sample	Vysoké Mýto			Holešov-Žopy		
	Layer			Layer		
	0–1 cm	1–2 cm	2–3 cm	0–1 cm	1–2 cm	2–3 cm
Specific surface area (m/g)	14.805	12.695	8.742	9.417	8.184	6.638
Total cumulative volume (cc/g)	0.239	0.216	0.230	0.228	0.242	0.194
Total porosity (%)	39.861	43.273	43.023	41.692	48.870	37.246
Bulk density (g/cm^3)	1.665	2.006	1.868	1.829	2.021	1.917

$CaCl_2$ (99% purity) from Lach-Ner Ltd. (Prague, Czech Republic) was used in the experiment. The concentration of the $CaCl_2$ solution was chosen to be 10 g/L based on previous laboratory experiments. The solution was prepared by dissolving appropriate amounts of $CaCl_2$ powder in distilled water.

A two-compartment box made of plexiglass was used (see Figure 4). Initially, dry brick discs were sealed with silicone in a circular aperture cut in the plexiglass panel, splitting the box into two chambers. One of the chambers (chamber 1) was filled with 500 mL of distilled water, while the other chamber (chamber 2) was filled with calcium solution of the desired concentration (500 mL).

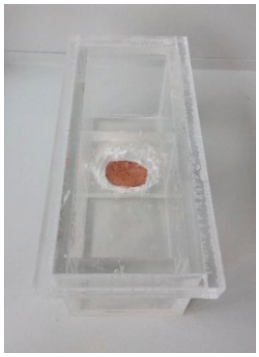

Figure 4. One of the model plexiglass boxes for experiments with calcium diffusion.

The box was closed with a plexiglass lid. The box was placed on a table at the ambient temperature of 20 ± 2 °C for a period of 240 h. The amount of calcium diffused through the sample was measured in chamber 1 by titration in selected time periods (0–240 h). When

the accumulation started, the distilled water was replaced by the same new water and these replacements were conducted after each measuring of calcium concentrations.

A 0.05 M solution of chelaton III was used to measure the calcium concentration. Namely 500 µL of a 5 M solution of KOH was added to a specific amount of the monitored aquatic sample from chamber 1 and colored using a murexide indicator. Chelaton III was then dripped into the sample by an automatic burette [12]. A specific amount of titration reagent was used to calculate the calcium concentration c(Ca) in mg/L, according to the following Equation (1):

$$c(Ca)\left(\frac{mg}{L}\right) = \frac{V(ch).M(ch).\,M(Ca).1000}{V(sample)} \quad (1)$$

where:

V(ch) is the volume of used chelaton (mL);
M(ch) = 0.05 is its molarity;
M(Ca) = 40 g/mol is the calcium molar mass;
V(sample) is the volume of the analyzed aquatic sample (mL).

The disks from all of the studied brick layers (0–1 cm, 1–2 cm and 2–3 cm) from the two bricks were used. Every disc was separately placed in distilled water (V = 100 mL) in a glass vessel and left at a temperature of 20 ± 2 °C and under the illumination of 5000 LUX intensity in a light–dark period of 12:12. No organisms were added to the water. The samples were left in order for natural bio-colonization to occur on their surface. The samples were immersed in water for 30 days. They were then pulled out of the solutions and photographed. The biofilm scraped from the samples was then examined under the light microscope Olympus BX43 (Olympus, Prague, Czech Republic) with a CMOS camera (magnification 400×). The brick disks of the individual layers were then put into the glass test vessels into a 100 mL volume of distilled water. The test vessels were left at a temperature of 20 ± 2 °C and under the illumination of 5000 LUX intensity in a light-dark period of 12:12 for a time period of 168 h. The biomass of the biofilm was measured using a VIS spectrometer (under 680 nm of wavelength) (Thermo Fisher Scientific, Prague, Czech Republic).

3. Results

Table 2 shows the different rate of calcium diffusion through the samples. The intensity of calcium diffusion was higher for the Vysoké Mýto sample and the diffusion of calcium through this sample began during the first 24 h of the experiment. Calcium diffusion through the Holešov-Žopy sample began one day later and the diffusion was less intensive. The diffusion took place faster on the surface (0–1 cm) than in the core of the bricks (2–3 cm).

Table 2. Diffusion experiment with the Vysoké Mýto and Holešov-Žopy bricks. The results are expressed as a cumulation of calcium in distilled water over the time period.

Sample	**Vysoké Mýto**			**Holešov-Žopy**		
	Calcium Concentration in the Distilled Water (mg/L)					
	Layer			**Layer**		
	0–1 cm	**1–2 cm**	**2–3 cm**	**0–1 cm**	**1–2 cm**	**2–3 cm**
Time						
24	40	20	30	0	0	0
48	180	135	148	80	80	80
72	298	220	266	150	153	164
168	802	726	711	498	466	414
192	1160	1011	912	558	516	449
216	1260	1228	1198	678	616	509
240	1546	1416	1201	1078	912	709

The photographs from the biological experiment (Figures 5–8) confirmed that both types of bricks and all their investigated layers were very intensively covered by microorganisms The composition of biofilm was observed under a microscope (Figures 6 and 8). Both samples were covered by a mix of algae and cyanobacterial species. The density of the biofilm was expressed as an absorbance (see Table 3). The absorbance values were the highest for the surface layer of bricks (0–1 cm). The highest difference was found for the 2–3 cm layer where the two kinds of brick should be considered.

Figure 5. Samples of the Vysoké Mýto bricks covered by a biofilm layer of 0–1 cm, 1–2 cm and 2–3 cm (from left to right).

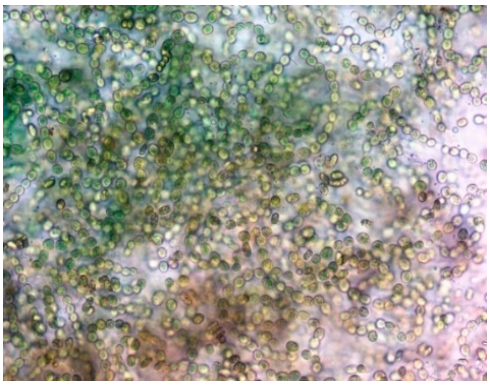

Figure 6. Biofilm on the surface of the Vysoké Mýto bricks. A photo was taken under the light microscope Olympus BX43 with a CMOS camera (magnification 400×).

Figure 7. Samples of the Holešov-Žopy bricks covered by a biofilm layer of 0–1 cm, 1–2 cm and 2–3 cm (from left to right).

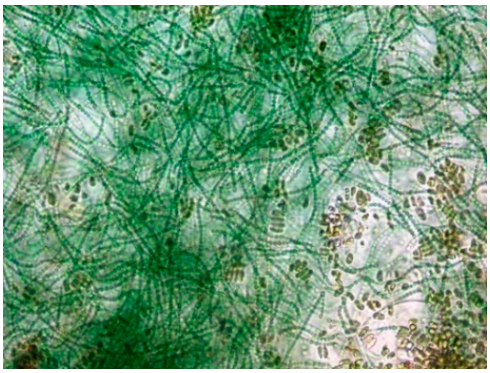

Figure 8. Biofilm on the surface of the Holešov-Žopy bricks. The photo was taken under the light microscope Olympus BX43 with a CMOS camera (magnification 400×).

Table 3. Biological experiment with the Vysoké Mýto and Holešov-Žopy bricks. Biofilm density on the surface of samples expressed by absorbance values.

Sample	Vysoké Mýto			Holešov-Žopy		
	Layer			Layer		
	0–1 cm	1–2 cm	2–3 cm	0–1 cm	1–2 cm	2–3 cm
Replicate	Absorbance [A]					
1.	0.247	0.112	0.143	0.262	0.105	0.060
2.	0.244	0.112	0.141	0.263	0.113	0.066
3.	0.244	0.113	0.147	0.269	0.116	0.069
mean	0.246	0.113	0.145	0.266	0.110	0.066
SD	0.002	0.006	0.004	0.004	0.006	0.005

4. Discussion

Calcium diffusion through bricks has never been studied, with the exception of a study where calcium was used to detect the age of bricks [19]. For this reason, we are not able to compare our results with the data from the literature. However, calcium diffusion was studied for sandstone [6,20]. Calcium diffusion for the Holešov-Žopy sample was relatively similar to calcium diffusion through the Mšené sandstone, but the Vysoké Mýto sample caused higher diffusion than the sandstone by about one-fifth during the same time period. In the case of sandstone, in the sample from the Hořice locality, calcium diffusion was about one order of magnitude lower. These discrepancies are affected by the composition of the studied building materials and their physical–chemical properties. Moreover, the sandstones by themselves are a highly variable group of rocks with a wide range of physical properties.

The microstructure of brick samples may be described by several metrices, which are obviously interrelated. The highest and positive correlation between the increasing intensity of diffusion and an increasing specific surface area was observed (Table 1). It may indicate that the diffusion of chlorides is taking place by a surface diffusion mechanism where chloride ions are adsorbed on the brick surface. The Vysoké Mýto brick has lower differences in percentage composition between individual layers than the Holešov-Žopy brick; the total porosity of the Vysoké Mýto sample was from 40 to 43% of all the studied layers while the Holešov-Žopy sample had a total porosity of 42% (0–1 cm), 49% (1–2 cm) and 37% (2–3 cm). This fact could have significance not only for diffusion but also for biofilm density. The Holešov-Žopy brick also has a greater amount of the highest pores (10–100 μm).

Bio-colonization of buildings is affected by moisture and nutrient availability, favorable pH, essential and trace metal availability and suitable solar radiation, e.g., Ref. [20]. Biodegradation of bricks was studied many times [21] but species diversity and abundance

have never been studied in depth among the individual layers in the bricks. In the present study, the bricks' layers were completely immersed in water to accelerate the growth of the biofilm and it was clearly visible both on the surface of the bricks and in the surrounding water. The biofilm coatings were photographed, and their analysis shows the presence of cyanobacteria and green algae. At least two species were observed microscopically in both types of bricks and their layers (Figures 6 and 8). These conclusions seem to be logical, and it likely cannot be assumed that more species of these organisms would be present in the depths.

The samples contained unicellular and multicellular organisms and it is therefore not possible to clearly determine the number of cells in the solution. The density of the organisms was indirectly expressed spectrometrically, but we did not recalculate the absorbance values on cell density for any volume unit. The density of the biofilm was once again higher in the samples with a higher visual porosity (0–1 cm layers) and for the Vysoké Mýto sample than for the Holešov-Žopy sample. Such broken surfaces and crevices probably allow algae to colonize the surface of building materials more intensively. The intensity of bio-colonization is more- or less-increasing with the rate of ions diffusion in the material as well as with the specific surface area. It again indicates that colonies are partially controlled by the available surface of the material.

5. Conclusions

Two fired bricks (Vysoké Mýto sample and Holešov-Žopy sample) were cut and their layers were studied in a diffusion experiment with calcium or in a biodegradation experiment. The results indicated that the structure of bricks' layers and especially their specific surface area affected the rate of calcium diffusion through the brick layers and probably also the density of colonization by biofilm (algae, cyanobacteria).

Author Contributions: Conceptualization, K.K and I.M. and R.Č.; methodology, K.K. and J.N. and M.K. and I.M..; investigation, K.K.; writing—original draft preparation, K.K. and M.K. and Z.S. and R.Č.; writing—review and editing, K.K. and Z.S. and R.Č.; supervision, R.Č. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Czech Technical University, grants No. SGS19/143/OHK1/3T/11, SGS22/137/OHK1/3T/11, by Technological Agency of Czech Republic, grant No. FW03010422 and by the Ministry of Education, Science, Research and Sport of the Slovak Republic, project VEGA No. 1/0682/19.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data supporting the reported results can be found with the authors.

Acknowledgments: The authors would like to thank Magdaléna Doleželová for measuring of bricks' properties, native speaker Marek Procházka for correction of English and two anonymous reviewers for their valuable advice. Publication cost of this paper was covered with founds of the Polish National Agency for Academic Exchange (NAWA): "MATBUD'2023—Developing international scientific cooperation in the field of building materials engineering" BPI/WTP/2021/1/00002, MATBUD'2023.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gredmaier, L.; Banks, C.J.; Pearce, R.B. Calcium and Sulphur Distribution in Fired Clay Brick in the Presence of a Black Reduction Core Using Micro X-ray Fluorescence Mapping. Available online: https://core.ac.uk/download/pdf/1493405.pdf (accessed on 5 December 2022).
2. Pel, L.; Pishkari, R.; Casti, M. A simplified model for the combined wicking and evaporation of a NaCl solution in limestone. *Mater. Struct.* **2018**, *51*, 66. [CrossRef] [PubMed]
3. Ahl, J. Salt diffusion in brick structures—Part II—The effect of temperature, concentration and salt. *J. Mater. Sci.* **2004**, *39*, 4247–4254. [CrossRef]
4. Petkovic, J.; Huinink, H.P.; Pel, L.; Kopinga, K.; van Hees, R.P.J. Moisture and salt transport in three-layer plaster/substrate systems. *Constr. Build. Mater.* **2010**, *24*, 118–127. [CrossRef]

5. Pavlík, Z.; Michálek, P.; Pavlíková, M.; Kopecká, I.; Maxová, I.; Černý, R. Water and salt transport and storage properties of Mšené sandstone. *Constr. Build. Mater.* **2008**, *22*, 1736–1748. [CrossRef]
6. Kobetičová, K.; Keppert, M.; Medveď, I.; Nábělková, J.; Černý, R. Effect of sample prewetting on the diffusion of calcium in sandstone. In Proceedings of the 6th International Conference on Chemical Technology (ICCT), Mikulov, Czech Republic, 16–18 April 2018.
7. Medveď, I.; Kalvoda, L.; Vejmelková, E.; Vratislav, S.; Černý, R. Transport of gadolinium in a cement composite. In Proceedings of the 4th Central European Symposium on Building Physics (CESBP 2019), Prague, Czech Republic, 2–5 September 2019.
8. Medveď, I.; Černý, R. Modeling of radionuclide transport in porous media: A review of recent studies. *J. Nucl. Mater.* **2019**, *526*, 151765. [CrossRef]
9. Medveď, I.; Černý, R. Concentration Dependence of Diffusion Coefficients of Na-22(+) and Cs-134(+) In Opalinus Clay Rocks. In Proceedings of the International Conference on Numerical Analysis and Applied Mathematics (ICNAAM-2018), Rhodes, Greece, 13–18 September 2018.
10. Hlušek, J. Zásady Vápnění půd. Available online: http://web2.mendelu.cz/af_221_multitext/vyziva_rostlin/html/hnojiva/mineralni/cazasady.htm (accessed on 5 December 2022).
11. Coldsnow, K.D.; Relyea, R.A. The combined effects of macrophytes and three road salts on aquatic communities in outdoor mesocosms. *Environ. Pollut.* **2021**, *287*, 117652. [CrossRef]
12. *ČSN ISO 6058 (757416)*; Jakost vod. Stanovení vápníku. Odměrná metoda s EDTA. Český normalizační institut (ČNI): Prague, Czech republic, 1996.
13. Gaylarde, C.C.; Gaylarde, P.M. A comparative study of the major microbial biomass of biofilms on exteriors of buildings in Europe and Latin America. *Int. Biodeterior. Biodegrad.* **2005**, *55*, 131–139. [CrossRef]
14. Quagliarini, E.; Gianangeli, A.; D'Orazio, M.; Gregorini, B.; Osimani, A.; Aquilanti, L.; Clementi, F. Effect of temperature and relative humidity on algae biofouling on different fired brick surfaces. *Constr. Build. Mater.* **2019**, *199*, 396–405. [CrossRef]
15. Gutarowska, B.; Celikkol-Aydin, S.; Bonifay, V.; Otlewska, A.; Aydin, E.; Oldham, A.L.; Brauer, J.I.; Duncan, K.E.; Adamiak, J.; Sunner, J.A. Metabolomic and high-throughput sequencing analysis-modern approach for the assessment of biodeterioration of materials from historic buildings. *Front. Microbiol.* **2015**, *6*, 979. [CrossRef]
16. Prohlášení o vlastnostech. Available online: https://cihelna.hrabcuk.cz/cs/dokumenty-ke-stazeni (accessed on 5 January 2023).
17. Prohlášení o vlastnostech. Available online: http://www.cihelny-zlinsko.cz/files/modules/products//1/files/certifikat-vyrobku-zopy_516257b59d9dc.pdf (accessed on 5 January 2023).
18. Waddell, C.; Fountain, J.C. Calcium diffusion: A new dating method for archeological materials. *Geology* **1984**, *12*, 24–26. [CrossRef]
19. Kobetičová, K.; Medveď, I.; Keppert, M.; Černý, R. Measurement and Modelling of Calcium Diffusion in a Sandstone. In Proceedings of the Thermophysics 2018, Smolenice, Slovakia, 7–9 October 2018.
20. Munyai, T.; Songishe, T.; Gumbo, J. Algae colonisation of brick pavement at the University of Venda: A potential slippery hazard. *Jamba J. Disaster Risk Stud.* **2019**, *11*, 1–7. [CrossRef] [PubMed]
21. Wilimzig, M. Biodeterioration of building materials like brick and mortar. *Int. Biodeterior. Biodegrad.* **1996**, *133*, 177–183.