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Assessing the Durability of Coastal High-Performance Concrete (HPC) Structures Exposed to Biodegradables such as Algae and Moss

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ABSTRACT

Coastal High-Performance Concrete (HPC) structures face deterioration challenges from exposure to biodegradables like algae and moss. This study examined the durability of coastal HPC under these biodegradable influences, emphasizing their effects on various transport properties. Conducted over 2 years in the environmentally rigorous Bandar Anzali Ports, the research evaluated key HPC transport properties such as water absorption, Rapid Chloride Penetration Test (RCPT), Rapid Chloride Migration Test (RCMT), electrical resistivity, and freeze-thaw resistance. Experimental samples, replicating real-world coastal conditions, incorporated diverse algae and moss concentrations. The comprehensive testing indicated that algae and moss presence notably hastened HPC degradation. Samples exposed to these organisms demonstrated increased water absorption, evidenced by weight gain. Enhanced chloride penetration and migration were evident from RCPT and RCMT results, suggesting an elevated corrosion risk in the concrete structures. Moreover, a marked drop in electrical resistivity indicated reduced concrete capacity to impede electrical current, while freeze-thaw tests showed heightened damage vulnerability from cyclic freezing and thawing. In light of these findings, it's crucial to address the biodegradable impact on coastal HPC structures. Implementing strategies like routine cleaning and maintenance to reduce algae and moss, combined with appropriate surface treatments, can extend the lifespan of coastal concrete installations. These insights aid in creating resilient and sustainable concrete mixes specific to coastal applications, ensuring extended structure longevity and integrity.

Keywords: Coastal structures, High-Performance Concrete (HPC), algae, moss, durability

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1. INTRODUCTION

With approximately 70% of the Earth's surface covered by oceans, the marine environment plays a crucial role in global ecosystems. Marine reinforced concrete structures are commonly affected by severe marine environmental conditions, leading to early deterioration primarily caused by chloride attack. This rapid corrosion of steel bars reduces the cross-sectional area of reinforcement, resulting in a decline in the structural performance of concrete structures.

The penetration of chloride ions into concrete during chloride-induced corrosion has been extensively discussed worldwide, but it remains a contentious topic. To accurately assess the lifespan of a structure, it is essential to develop a dependable predictive model for chloride ion penetration in concrete. While various models have been proposed in research, the practical prediction typically employs the error function solution to Fick's second law. The mechanisms of chloride ion penetration are intricate due to the involvement of multiple factors, such as the interaction between chloride and cement hydrates, moisture conditions of the concrete, and the time-dependent diffusion coefficient, among others. Furthermore, the penetration process in concrete immersed in real seawater differs from that in a simulated sodium chloride solution. For instance, interactions between cement hydrates and minor ions in seawater can lead to the formation of a surface skin composed of a thin layer of brucite, approximately 30 µm thick, overlaying a thicker layer of aragonite. This surface skin significantly reduces the permeability of the concrete. Advanced predictive models that consider these phenomena are currently being developed. Additionally, marine structures exposed to tidal and submerged environments often become covered with a multitude of marine organisms, such as algae, moss, oysters, and mussels. The attachment of these marine organisms is considered undesirable from an aesthetic perspective, and they are commonly referred to as "marine fouling organisms." Moreover, these marine organisms obstruct the visual inspection of the structure, leading to misleading inspection results. Therefore, during inspections of existing marine structures, removing marine organisms from the concrete surface is necessary when required. Among the essential herbivores in the ocean are phytoplankton and benthic algae. Marine algae, commonly known as seaweeds, represent a diverse group of photoautotrophic organisms that exhibit various shapes and contain pigments such as chlorophyll, carotenoids, and xanthophylls. Coastal areas, characterized by sandy beaches, offer ideal conditions for the abundant growth of marine algae due to the availability of attachment points in the dynamic environment of the shoreline [1-8].

In coastal environments, the initial attachment of plant life to structures is typically observed in the form of filamentous macroalgae. The constant abrasion caused by tidal action lifting sand and small stones around the base of these structures promotes colonization by these organisms. While several seaweed species can be found in such environments, dominant species like algae often prevail. These green algae belong to the phylum Chlorophyta and are commonly observed attached to rocky and concrete substrates near the ocean's surface, avoiding being washed up on the beach by waves. Macroalgae possess the ability to obtain essential elements for their metabolism, such as calcium, aluminum, silicon, and iron, through the process of bio-solubilization. This process involves the production of organic acids as a result of macroalgae's metabolic activity. However, this acid deterioration is a well-known biogeochemical mechanism that contributes to the decay of concrete structures. To comprehend the terminology and chemical processes involved, it is essential to explore the following concepts:

Biogeochemical Deterioration Mechanism: The release of corrosive acids produced by living organisms or biological processes is a prominent and extensively studied biogeochemical damage mechanism in inorganic materials like concrete. This process, known as biocorrosion, occurs due to the microbial secretion of inorganic and organic acids through acidolysis and complexation, leading to the leaching of the mineral matrix and subsequent weakening of the binding system [9-12].

Biocorrosion: Biofilms, which are structured communities of microorganisms encapsulated within a self-developed polymeric matrix adhering to surfaces, can influence the kinetics of corrosion processes. The metabolic byproducts of biofilms, including enzymes, exopolymers, organic and inorganic acids, as well as volatile compounds like ammonia or hydrogen sulfide, can alter electrochemistry at the biofilm/metal interface, affecting cathodic and anodic reactions. This phenomenon is commonly referred to as "biocorrosion" or "microbially influenced corrosion" (MIC). Biodeterioration refers to any undesirable change in the properties of a material caused by the vital activities of organisms. Phytochemistry, on the other hand, focuses on the study of natural products and chemical constituents found within algal thalli from a biological perspective. These constituents encompass various natural products such as saturated and unsaturated fatty acids, sterols, terpenoids, and sugars. In the context of this study, we aim to assess the impact of marine organisms, such as moss and algae on concrete structures in Bandar Anzali Ports.Fig1. Anzali Port, located in the north of Iran, houses numerous marine structures exposed to the coastal environment. These structures are susceptible to deterioration caused by macro flora present in seawater. Although considered a secondary deterioration process, the effect of this macro flora is significant. Algae growth is observed on concrete structures throughout the year due to favorable ambient conditions in the coastal area [13-16]. This study aims to investigate the effects of marine moss and algae growth on the durability of concrete structures. Concrete structures were immersed in the coastal area, where abundant algae growth was tested in laboratory conditions. Additionally, the phytochemical analysis of algae was conducted to identify the chemical constituents occurring in the algae as a result of secondary metabolites. The surfaces of the concrete cores were chipped to assess the extent of algae growth in terms of visual evaluation. This research aims to enhance our understanding of the deterioration mechanisms associated with the presence of algae on concrete structures and contribute to the development of effective strategies for mitigating such deterioration.

Figure 1. The proliferation of marine organisms on concrete components

2. MATERIALS AND METHODS

2.1. Concrete Mix Designs

The objective of this study was to present a detailed description of the concrete mix design utilized in the construction of coastal structures and to outline the methodology adopted for evaluating the soundness of this concrete after a decade of service. The concrete mix design used in the rehabilitation of the studied coastal structures was sourced from prior documentation provided by the ports organization. The specific constituents of the mix design are presented in Table 1. This mix was aimed to achieve a target compressive strength of 50 MPa.

Table1. Mix component for the existent coastal concrete retaining wall

Concrete type	**Cement (kg/m^3)**	**Water (kg/m^3)**	**Silica Fume (kg/m^3)**	**Sand 0-4.75 (kg/m^3)**	**Gravel 4.75 -25 (kg/m^3)**	**Super Plasticizer (kg/m^3)**
Coastal Existence Mix	380	165	20	350	650	1.4

To assess the long-term durability and structural integrity of the structures made using the aforementioned mix design, core samples were extracted. The core extraction focused on obtaining samples from areas of the structure that were either beneath or directly exposed to biodegradables like algae and moss. This approach was taken to specifically gauge the effects of these organisms on the concrete's durability. Core samples were systematically taken from various critical points on the structure, ensuring a comprehensive representation of the structure's entirety. These samples were then prepared for subsequent analysis, focusing on assessing potential degradation, such as corrosion, cracking, or other signs of distress that might compromise structural integrity.

2.2. Methods

2.2.1. In-situ Testing

A potential corrosion mapping of the concrete elements covered by algae and moss was performed using a Gecor 10 instrument, which is utilized for non-destructive corrosion monitoring in reinforced concrete structures. The mapping was conducted with a mesh size of 2 × 2 m^2, enabling surface inspection of the selected elements in batches. A Cu/CuSO4 electrode was employed to measure corrosion potential. Corrosion potential values more positive than -270 mV indicated a low probability of corrosion, while values more negative than -420 mV indicated a high probability of corrosion. Resistivity (ρ) measurements were simultaneously taken with corrosion potential measurements. Resistivity values below 100 Ωm were considered to pose a high risk of corrosion, while values above 1000 Ωm indicated a low risk of corrosion. A comprehensive overview of commonly used non-destructive corrosion determination methods for reinforced concrete was considered. Non-destructive methods offer advantages over destructive methods, such as continuous monitoring of reinforcement conditions, measurements at the structural level, and cost-effectiveness. However, the determination of reinforcement steel with non-destructive methods can be complex and may lead to incorrect interpretations. To mitigate misinterpretations, it is recommended to combine multiple non-destructive testing methods before drawing conclusions about reinforcement steel corrosion.

2.2.2. Laboratory Tests

Thirty core samples with a diameter of 100 mm and an approximate length of 200 mm were extracted for laboratory testing. Among these, three cores were obtained from areas covered by algae and moss, while three more cores were extracted from buttresses exposed only to humidity without any algae. Core samples were collected from five zones with a minimum distance of 2 meters between them.

All concrete core samples underwent the following measurements:

- Visual Inspection: The cores were visually inspected to assess the extent of algae and moss growth and any visible signs of deterioration.
- Chloride Profile: The chloride profile of the concrete cores was determined according to EN 12390-11, which involves extracting samples at different depths and analyzing the chloride content to evaluate the extent of chloride ingress.
- Water Penetration Depth under Pressure: Water penetration depth under pressure was determined following the procedure outlined in EN 12390-8, which involves subjecting the cores to pressurized water and measuring the depth of water penetration to assess the concrete's resistance to water ingress.
- Electrical Resistivity of Concrete: The electrical resistivity of the concrete was measured according to AASHTO T358, providing an indication of the concrete's ability to resist the passage of electrical current and its potential durability.
- Mercury Intrusion Porosimetry: Mercury intrusion porosimetry, following ASTM D4404, was conducted to evaluate the pore size distribution and porosity characteristics of the concrete, providing insights into its

permeability and susceptibility to moisture ingress.

By conducting these laboratory tests, a comprehensive assessment of the concrete's condition, including its visual appearance, chloride ingress, water penetration resistance, electrical resistivity, and pore characteristics, will be obtained. These tests will provide valuable insights into the effects of algae and moss on the durability of the concrete structures in the Bandar Anzali Ports.

2.2.3. Mineralogical Characterization

Mineralogical characterization of algae and moss involves studying the mineral composition and properties of these organisms, which are known for their ability to thrive in diverse environments, including aquatic and terrestrial habitats. Algae, a group of photosynthetic organisms that range from single-celled microalgae to complex multicellular seaweeds, exhibit a wide variety of mineralogical characteristics. Certain algae, such as diatoms, produce intricate silica-based cell walls called frustules. These frustules have unique mineralogical properties, including diverse patterns and structures. Diatom frustules can be composed of amorphous silica, which is formed through a process known as biomineralization. The mineralogical properties of diatom frustules are of great interest in fields such as nanotechnology, materials science, and environmental monitoring. Other types of algae, such as coralline algae, are known to precipitate calcium carbonate, similar to coral reefs. These algae incorporate calcium carbonate minerals into their cell walls, providing structural support and protection. The mineral composition of coralline algae can vary, including forms of aragonite and high-magnesium calcite. Understanding the mineralogical characteristics of coralline algae contributes to the study of coral reef ecosystems, as these algae play significant roles in reef development and stabilization. Mosses, on the other hand, are small, non-vascular plants that can grow in a wide range of environments, including moist terrestrial habitats, rocks, and tree bark. While mosses are not known for their extensive mineralization, like some algae, they can interact with minerals in their surrounding environments. For instance, mosses can accumulate mineral particles from the air or water, incorporating them into their tissues. Some mosses are capable of accumulating heavy metals or other elements, which makes them useful as indicators of environmental pollution and monitoring.

The marine algae were gathered from the coastal region near Anzali port and underwent a thorough washing process to eliminate epiphytes, animal waste, attached debris, and sand particles. Subsequently, the algae were rinsed with distilled water and dried in the shade while being aerated to prevent the degradation of secondary compounds caused by sunlight and high temperatures. The dried algae were then cut and ground into smaller pieces. The following steps were carried out to extract the fatty acids from the dried algae:

ii. Extraction:

The dried, cut, and ground algae were immersed in methanol (MeOH) within a large glass container and left in the solvent for one month at room temperature. The resulting material extract was then filtered to remove any solid algae particles. Next, the extract was evaporated using a rotary evaporator under reduced pressure, resulting in a thick, dark green residue.

iii. Saponification:

A portion of the obtained extract was saponified by treating it with a solution of 10% potassium hydroxide (KOH) in 50% methanol, which was then refluxed at 100°C for six hours. The mixture was concentrated under reduced pressure, and water (H2O) and diethyl ether (Et2O) were added. After vigorous shaking, the Et2O layer was separated. The Et2O layer was evaporated and used for fatty acid analysis.

iv. Esterification:

All the fractions containing fatty acids obtained from the previous steps were subjected to methylation. This involved adding 1.5-2.0 mL of ethereal diazomethane to the mixture of fatty acids. The reaction mixture was left in the fuming chamber at room temperature overnight until it dissolved completely. The resulting aliquots were then directly injected into a Hewlett Packard gas chromatograph-mass spectrophotometer equipped with a computer system [17-20].

3. RESULT AND DISCUSSION

3.1. Capillary Water Absorption and Water Penetration Depth under Pressure

Figure 2 presents the final water absorption of all the samples. As per the CEB-FIP classification, concrete durability is categorized as poor, average, and good for water absorption values of 5% and above, 3-5%, and 0-3%, respectively. Notably, the HPC covered by algae and moss exhibited predominantly high-water absorption. Additionally, Figure 2 also demonstrates the final water absorption range for the concrete cores which are only in exposure of marine environment (without confining with algae and moss) is lower than algae-cover counterparts.

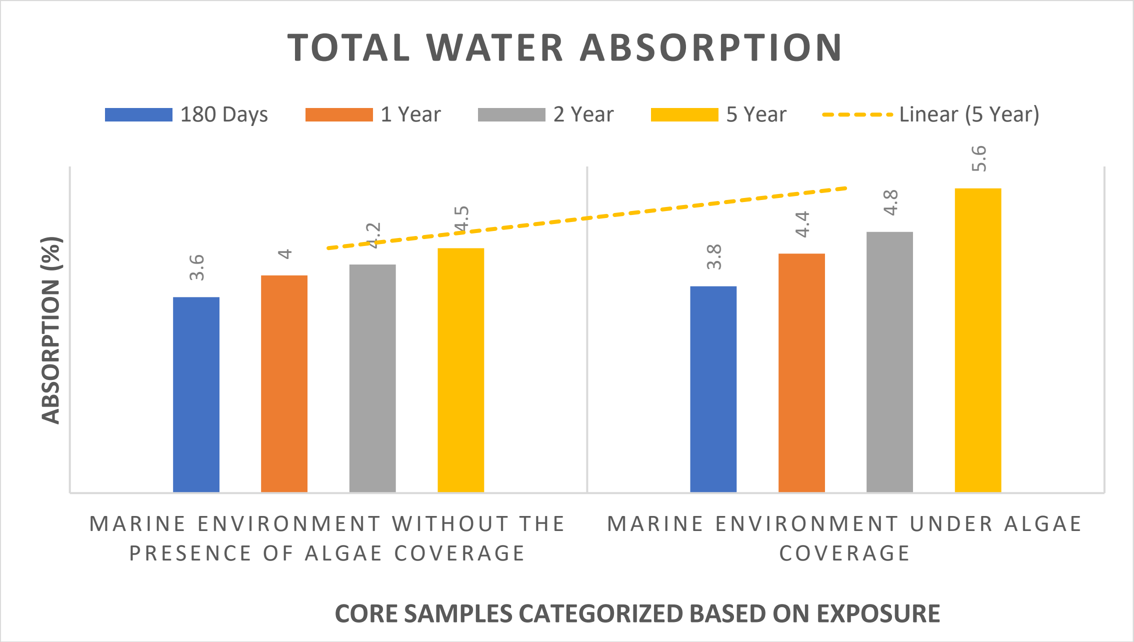

Figure 2. Final water absorption of marine concrete samples with/without algae coverage

Concrete cores with increasing algae and moss coverage content showed lower density and matrix compactness, consequently increasing the water absorption and permeability depth by up to 20 % after 2 years compared to mixtures without Algae Coverage. Table 2. This finding highlights the effectiveness of marine organisms in reducing impermeability under non-hydrostatic pressure (capillary water absorption) and hydrostatic pressure (water penetration depth) over time. The superior acid secretion of moss and algae contributes to reacting with the cementitious components of concrete, including silica (present in the form of amorphous silica or silicate minerals). The acids can dissolve or leach out the silica, leading to a decrease in silica levels on the concrete surface and causing more pores in the microstructure of concrete.

Table2. Depth of Penetration of marine concrete samples with/without algae coverage

Core samples	Depth of Penetration (mm)		
	90days	**1 year**	**2 years**
without Algae Coverage	15	17	20
With algae coverage	18	20	24

3.2. Electrical Resistivity

The surface resistivity test offers advantages such as affordability and ease of use, making it increasingly popular for assessing concrete's permeability properties. Electrical resistivity measurements were conducted on all concrete cores, and the corresponding results are presented in Figure 3.

Overall, the resistivity of the concrete mixtures increased with age, regardless of whether the marine organisms' coverage on them or not. In under algae and moss coverage, lower electrical resistivity can be observed.

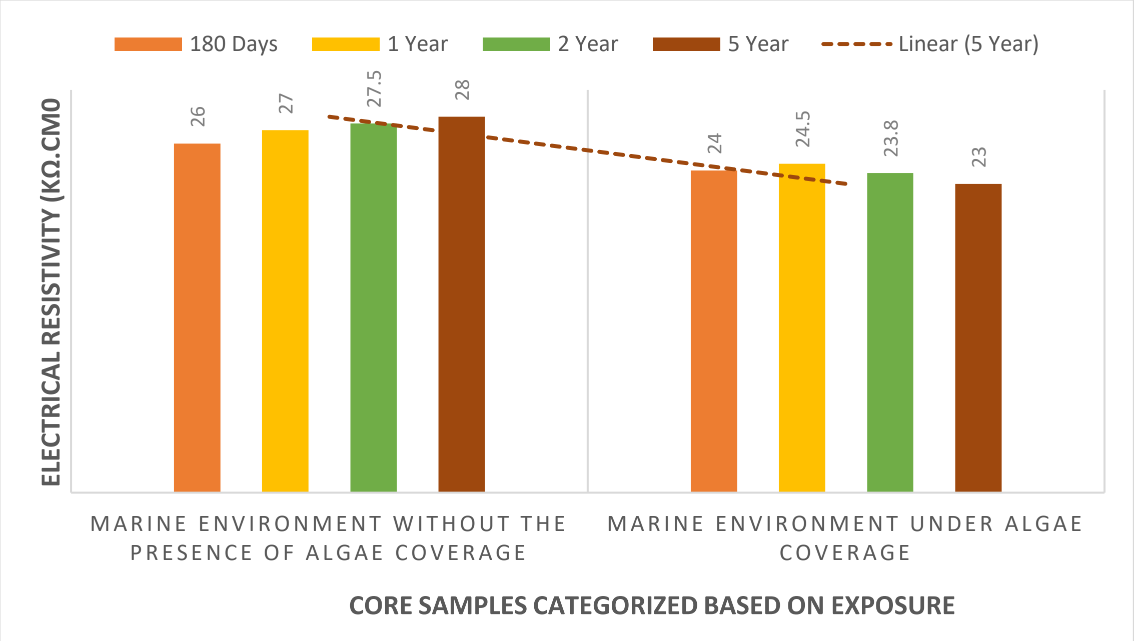

Figure 3. Electrical resistivity of marine concrete samples with/without algae coverage

3.3. Chloride Migration Profiles

The marine concrete mixtures developed in this study underwent chloride migration potential using RCMT (Rapid Chloride Migration Test). The results from RCMT were consistent with the findings from the surface resistivity test. Figure 4 presents the RCMT results for all cores with varying algae coverage in different ages. The figure illustrates that the rate of chloride migration into the cores with algae coverage is a little more than concrete samples without algae coverage. The chloride migration threshold, which indicates the critical level of chloride content required to initiate corrosion-induced deterioration near the steel reinforcement, must be taken into consideration. Based on the results, corrosion did not exceed the threshold migration level (17×10^{-12} m^2/s) in all marine cores, even with a maximum coverage of algae and moss.

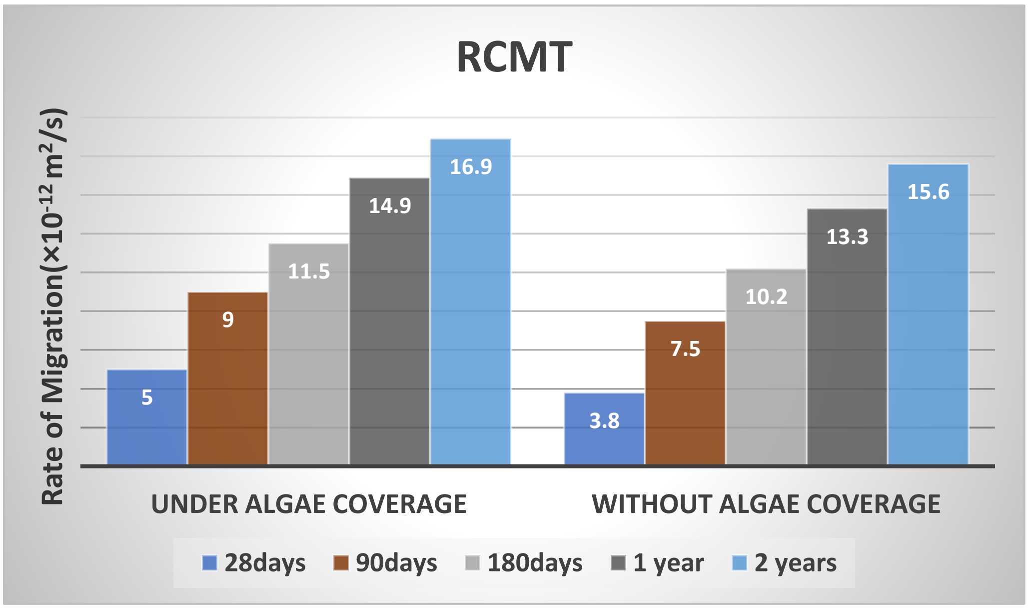

Figure 4. Chloride migration coefficient of marine concrete samples with/without algae coverage

3.4. Mercury intrusion porosimetry

The samples were analyzed, and the results showed that the average pore diameter ranged from 0.030 to 0.05 µm for the noncoverage and algae-coverage core samples. The density was measured at 2.10 g/ml, and a 150 to 200 MPa pressure was applied. This pressure led to total porosity ranging from 10 to 16% for the noncoverage and algae-coverage core samples, indicating medium permeability in both cases. As the pressure increased, the filling process occurred in progressively smaller pores. The technique employed in this analysis allows the characterization of both inter-particle pores (between individual particles) and intra-particle pores (within the particles themselves). The results indicated that the secretion of organic acids by moss and algae could dissolve silica particles, resulting in an increase in both inter and intra-pore sizes.

4. CONCLUSION

Algae and moss growth on the surface of concrete can contribute to reducing concrete density and concentration and facilitating the penetration of corrosive liquids. Here's an explanation of the processes involved:

- Organic acid secretion: Algae and moss can secrete organic acids as part of their metabolic activity. These organic acids can react with the cementitious components of concrete, including silica (present in the form of amorphous silica or silicate minerals). The acids can dissolve or leach out the silica, leading to a decrease in silica levels on the concrete surface.
- Acidic pH environment: Algae and moss growth can create an acidic microenvironment on the concrete surface due to the secretion of organic acids. This acidic pH environment can further enhance the dissolution of silica. Silica is more soluble under acidic conditions, and prolonged exposure to low pH can contribute to the leaching or dissolution of silica from the concrete surface.
- Utilization of portlandite: Portlandite (calcium hydroxide) is a byproduct of the hydration process in cementitious materials. It is commonly present in concrete. Research has shown that the portlandite crystals are absent in the presence of algae, indicating that the algae have utilized the portlandite for their metabolic activities. Algae can utilize the calcium ions from portlandite to support their growth and metabolic processes, resulting in the alteration or consumption of portlandite within the concrete.
- Physical disruption: The growth of algae and moss on the concrete surface can physically penetrate and disrupt the concrete matrix. The root-like structures or filaments of these organisms can create channels or openings within the concrete, which can lead to the loss or removal of silica-rich regions and portlandite crystals.

Overall, the combination of organic acid secretion, acidic pH environment, utilization of portlandite, and physical disruption caused by algae and moss growth can significantly alter the base material of concrete. These factors contribute to the decrease in silica levels and the absence of portlandite crystals, indicating the severe alteration of the concrete surface under algae and moss coverage. The combination of chemical reactions, moisture retention, and physical damage caused by algae and moss growth can result in reduced density and concentration of concrete. It weakens the concrete's structural integrity and makes it more susceptible to further deterioration from corrosive substances. Regular cleaning and maintenance to remove algae and moss growth are crucial for preventing these issues and preserving the durability of concrete structures.

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