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On the Impact of Algae on Accelerating the Biodeterioration/Biocorrosion of Reinforced Concrete: A Mechanistic Review

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Abstract

In this paper, the complexities involved in both microbiologically influenced corrosion and deterioration of reinforced concrete structures by algae are explained. In this regards, the five possible corrosion/deterioration mechanisms that may be expected are addressed and described. These mechanisms are as follows:

- Absorption of some chemicals necessary for the algae from within the cement paste of the concrete: this mechanism can finally result in drying out the concrete and developing cracks as a result of formation of internal cavities and voids.
- Biofilm formation and increasing the likelihood of attracting more micro-/macro-organisms that can either deteriorate the concrete itself or the reinforcement steel inside , or both. An example as such can be development of an environment favorable for the acid-producing sulphur oxidizing bacteria that through generating very acidic conditions are capable of doing harm to both metallic and non-metallic phases of the reinforced concrete.
- Development of electrochemical cells such as differential aeration cells due to the photosynthetic driven oxygen production and consumption features of algae. In

this way, it is likely that spots of varying oxygen partial pressures will be created, tus facilitating the corrosion of the steel inside.

- Production of acids that can be detrimental to the mechanical integrity of both concrete and steel reinforcement.
- Production of alkaline conditions that upon varying and fluctuating due to the chemistry of the system, can protect the concrete but do damage to the steel phase via mechanisms such as caustic embrittlement.

The aim of this review paper is to gather all possible mechanisms that may be involved in explaining the contribution of algae to the bio-corrosion/bio-deterioration of reinforced concrete.

Keywords: Microbiologically Influenced Corrosion (MIC)- Concrete-Steel- Algae-Biodeterioration-Biodegradation.

Introduction

An important phase in civil engineering applications is to protect the structure from the adverse effects of the surrounding environment on its integrity, durability and functionability. One important factor of such adverse impacts is deterioration of non-metals coupled with the corrosion of metallic structures[⊗] . One type of electrochemical corrosion is called "Microbiologically Influenced Corrosion" or briefly MIC.

Microbiologically influenced corrosion (MIC) has been defined in many ways in the related literature[1,2,3,4,5]. However, what is common among all these definitions are the following three points[6]:

1. MIC is an electrochemical process,
2. Micro-organisms are capable of affecting both the extent, severity and course of corrosion,
3. In addition to the presence of micro-organisms, an energy source, a carbon source, an electron donor, an electron acceptor and water also must be present to initiate MIC.

When it comes to such effects on non-metallic materials, one may use the same definition but replace "corrosion" with "deterioration". Therefore, Microbiologically Influenced Deterioration (MID) addresses the degradation/deterioration of non-metals as affected by micro-organisms.

In civil engineering applications one of the most used materials is concrete. Either as reinforced concrete-often with carbon steel as the reinforcement metallic phase- or plain concrete. MID is not a new terminology; in their 2003 paper, Rogers et al[7] addressed the importance of MID by saying "*an understanding of concrete degradation may be incomplete without in-cluding the effects of microbial influenced degradation, or briefly, MID*".

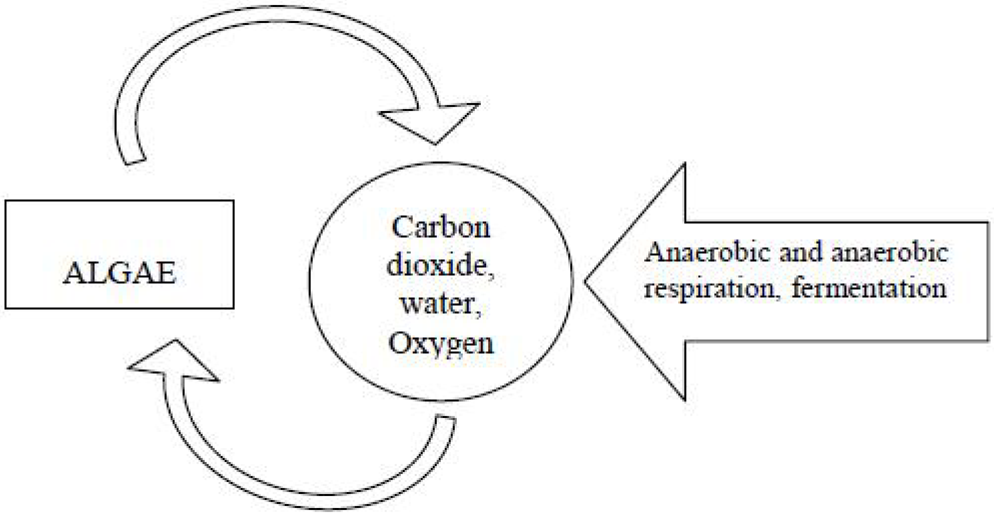
Concrete is a vulnerable material when it comes to MID[8,9,10] specially by algae[11]. However, it must be noted that the MID of concrete has been mainly addressed with regards to the impact of corrosion-enhancing bacteria such as sulphate reducing bacteria and sulphur oxidising bacteria[6]. In this review, we will focus mainly on the possible deteriorating effect of algae on concrete.

Algae are a diverse group of photosynthetic organisms ranging from microscopic single-cell micro-organisms to very large organisms such as seaweed[12]. In understanding the possible deterioration mechanisms stimulated by algae, the key element is to focus on their photosynthetic nature.

Photosynthesis is a process during which the atmospheric carbon dioxide is converted to organic carbon, as schematically shown in Figure 1:

[⊗] Conventionally, corrosion is used for metals and deterioration or degradation for non-metals.However, concrete corrosion can be taken to actually refer to the deterioration of concrete (non-metal) coupled with the corrosion of the steel reinforcement (metallic material).

Figure 1: Simplified photosynthesis chemical path and the role of algae in it. Through aerobic respiration (by animals, protozoans, plants and algae) and anaerobic respiration and fermentation (by fungi and bacteria), carbon dioxide, water and oxygen are generated. These chemicals are then used by other organisms-including algae.



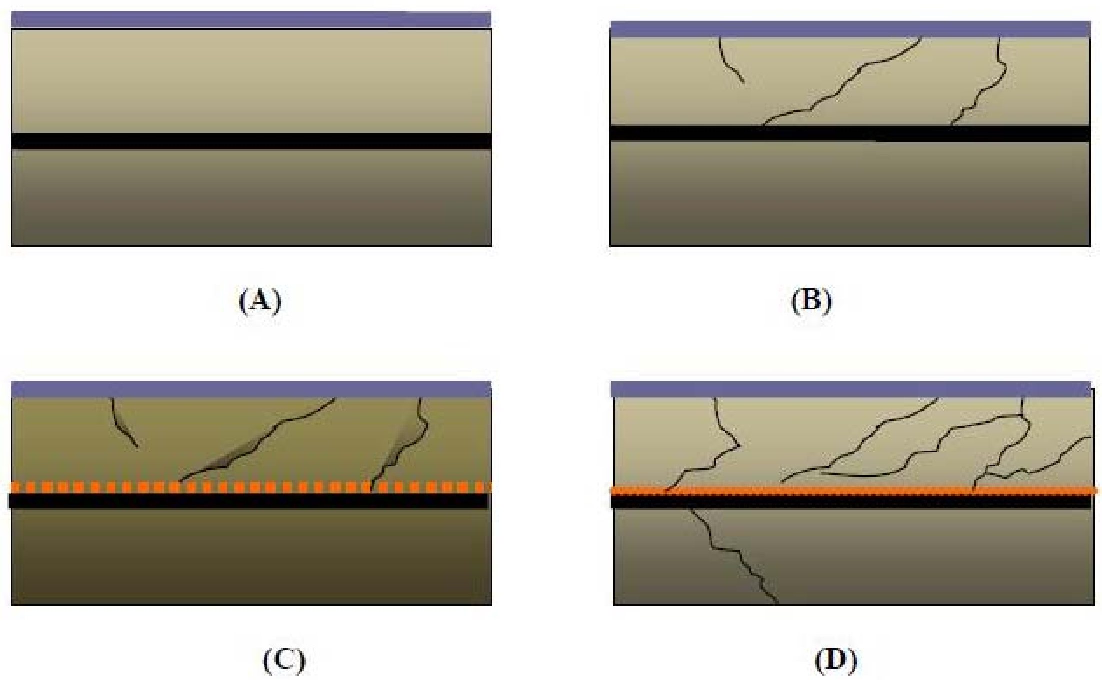
During photosynthesis carbon dioxide and water produce glucose and oxygen. It is this oxygen that can play an important role in one of the possible scenarios for the deterioration of concrete.

Corrosion Scenarios for the reinforced concrete:

To explain the possible contribution of algae to the corrosion-deterioration of reinforced concrete, one must take into the consideration the very important distinction we made between the use of MIC and MID. Algae can help both MID of the concrete phase and MIC of the steel phase of the reinforced concrete.

Figure 2 illustrates Tuutti's model. In this model the reinforced concrete is assumed to go through two stages[13] i.e. (1) initiation (where the embedded steel is still passive while corrosive mechanisms are active in the non-metallic phase) and (2) propagation (when the corrosion extent in the non-metallic phase reaches the steel and depassivate the steel so that corrosion starts to propagate at a significant rate).

Figure 2: One of the possible scenarios of reinforced concrete structures: (A) due to some "external factors" the outer surface of the concrete becomes conditioned so as to allow cracks develop internally (B). As the cracks develop, water ingress from outside can find its way deep into the reinforced metallic phase (C). Under these circumstances rust is developed (brown layer). The developed corrosion products (rust) in physical terms will need more space that can not be accommodated by the gap between the metallic phase and the concrete around it. The end-result is that, due to the internal tensile stresses thus produced, the non-metallic phase fails and cracks , thus allowing more water ingress by increasing the number of capillaries and cracks[14].

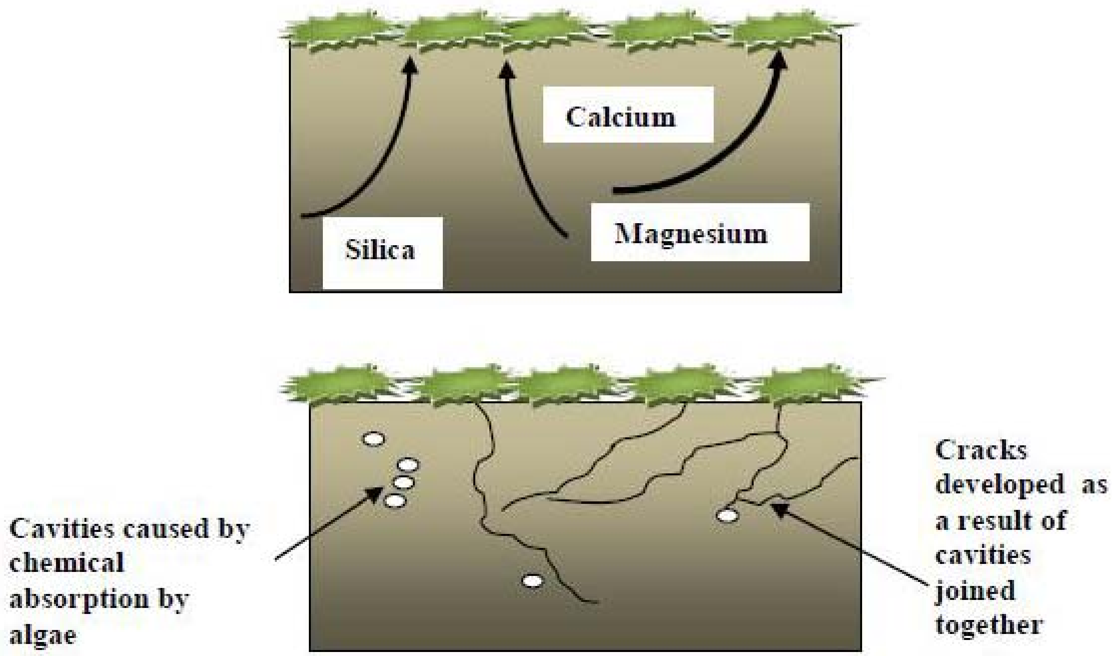


Obviously, when cracked are developed in the reinforced concrete structure, the steel inside starts to rust. the volume of the corroding steel reinforcement in terms of producing iron oxide will be increased by 2 to 4 times in comparison with non-corroded steel[12]. This increase in volume will produce internal tensile forces to which concrete is very weak. In a plain concrete structure, the developed cracks will help more water ingress. Due to factors such as temperature change, the trapped water in such capillaries starts to exert tensile stresses-in the same way that the rust does in reinforced concrete. The end result for both plain and reinforced concrete structures will be the loss of mechanical integrity of the structure and catastrophic failure.

As seen from the above, the critical step in the crack initiation-propagation corrosion-deterioration model is the crack initiation step. In other words, if somehow crack formation is favoured, the necessary step for the model to predict deterioration will be in place.

One of the ways by which algae can accelerate the MID of concrete is by taking some of the chemicals required for their metabolic processes out of the concrete (more specifically, from the cement paste)[15] . This process can be illustrated as Figure 3:

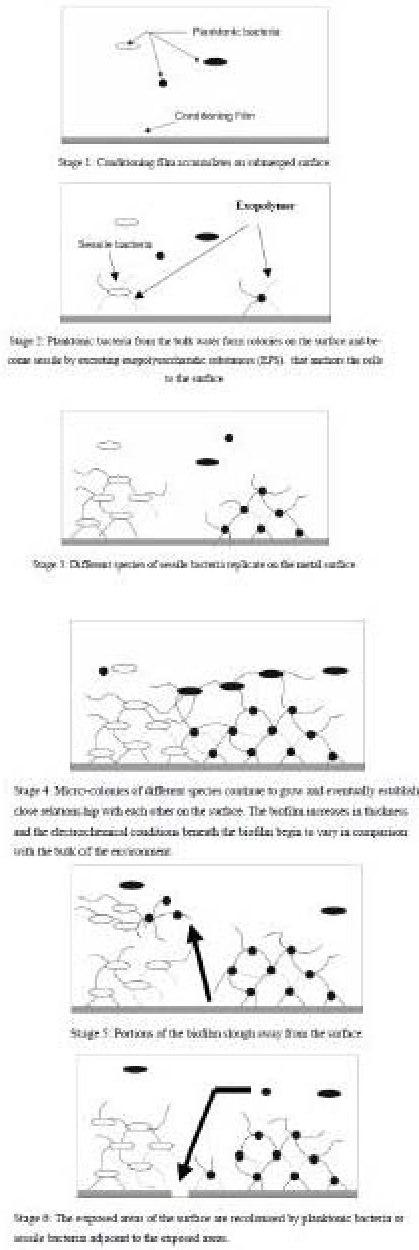
Figure 3: When algae are developed on concrete structures, they start to absorb chemicals such as calcium, silica and magnesium (Top). These chemicals will be taken out of the cement paste where small "cavities" and cracks will be generated (Bottom). These cavities will be the initiation sites for developing cracks.



By developing such small cavities in the body of the concrete, the crack initiation will be facilitated. Therefore, when cracks are initiated, the first stage of concrete deterioration according to Tuutti's model has been achieved. It is also important to note that algae can also act as the collection platform for other corrosion-related organisms such as fungi and bacteria, so that the deterioration process may gain momentum after the structure's conditions have become suitable for the survival of one of more such organisms. This brings us to the second possible scenario in which algae can play an important role in the MID of concrete - biofilm formation.

The second MID scenario stimulated by algae is that algae formed on the concrete surface can attract other organisms some of which can be quite corrosive. This collection of micro-organisms is called a biofilm which consists of cells immobilised at a substratum, frequently embedded in an organic polymer matrix of microbial origin[16] Biofilm formation is of a dynamic nature so that it is always going through a "built- ruined - rebuilt" cycle. Figure 4 schematically shows the steps involved in biofilm formation.

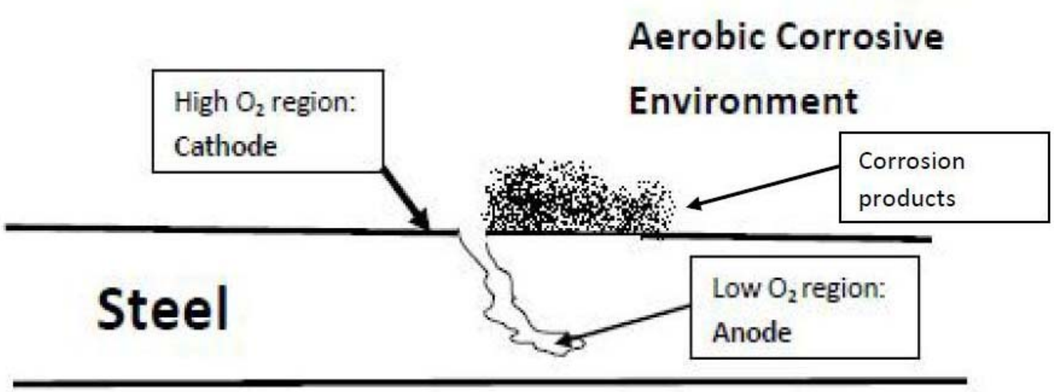
Figure 4: Stages involved in biofilm formation[6,17]



The existence of algae in a biofilm is a good indicator for expecting a diverse community of micro-organisms such as corrosion-enhancing bacteria, for instance, sulphate reducing bacteria (SRB). For SRB to become active, the conditions must be anaerobic, that is, free from oxygen. It has been shown that[18] a thickness of just 12 μm can make a local spot anaerobic enough for SRB activity in an aerobic system. In addition to the thickness of the biofilm that can prevent oxygen ingress to the base of the biofilm and thus make under-biofilm conditions anaerobic, oxygen-consuming organisms such as algae can also help form anaerobic environments by consuming the oxygen (in the absence of light) and thus eliminating other rivals-including themselves- for the benefit of SRB. It may also be possible that algae by photosynthesis can produce enough oxygen to help the growth of another type of corrosion-enhancing bacteria, the sulphur oxidising bacteria (SOB), which are aerobic and can co-exist with SRB. The cyclic impact of SRB and SOB on both MIC and MID of reinforced concrete structures have been discussed in length elsewhere[6,19].

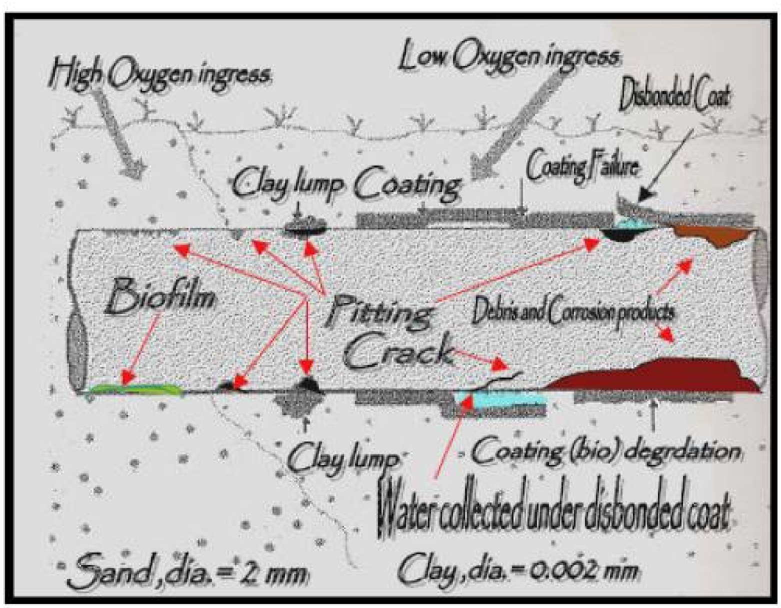
In order to explain the third possible scenario of MID by algae in concrete structures, we need to introduce a concept which is known in electrochemistry as "differential aeration cells". This concept simply says that if there are spots that receive different oxygen partial pressures, the anode will be formed where the oxygen pressure is the lowest. Figure 5 schematically shows an aeration differential cell due to formation of low and high oxygen partial pressures outside and within a crevice. More detailed explanations can be found elsewhere[20, 21].

Figure 5: Spots with low- and high- oxygen partial pressures can form anode and cathode inside and outside a crevice in a steel structure.



An example of the contribution of differential aeration cells to corrosion can be seen in buried pipelines where the pipe passes through two types of soils with different grain sizes that would provide different oxygen fluxes and thus establish an electrochemical cell where the anode (where pitting will happen) will be established at the spot with lower oxygen pressure. Figure 6 schematically shows an example of such instances. In addition to buried pipes, established differential aeration cells and their contributions to corrosion have been shown in other instances such as in process vessels and tanks at water-gas interface[22].

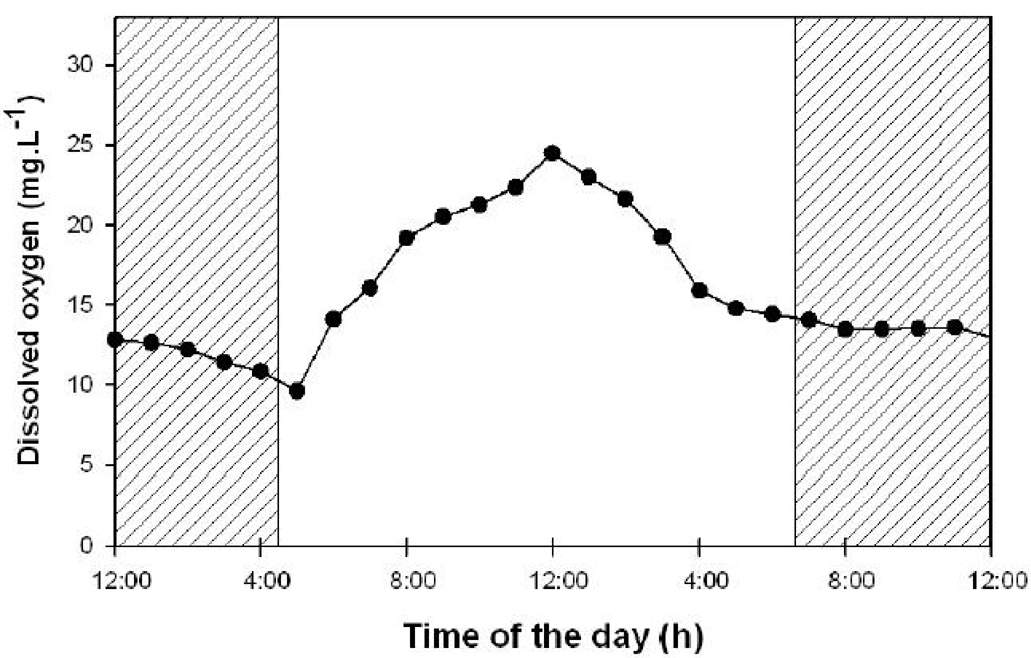
Figure 6: Due to difference in grain diameters, the part of the buried pipe which is exposed to the smaller oxygen ingress will become anodic with respect to the part that receives larger oxygen ingress[6].



Algae can contribute to the MIC of the reinforced steel phase in reinforced concrete structures, especially if they are exposed due to erosion-corrosion factors operating on the structure previously, via establishing differential aeration cells[23]. Due to photosynthetic nature of algae, these organisms can both produce oxygen in the light and consume it in the dark. This will create a cycle in which oxygen partial pressures will differ from spot to spot, thus increasing the risk of enhancing corrosion. Figure 7 shows change in oxygen concentration in a culture of marine algae over a 24 hour cycle. The algae will change the course of corrosion by establishing the electrochemical differential aeration cells and thus increasing the corrosion rate of the steel reinforcement in the concrete.

It is possible for the ferrous ions thus produced through the MIC of the reinforced steel phase further to affect the dynamics of the corrosion system. One way, in natural environments where different bacterial specices are available together, could be formation of a bacterial consortium that can have a more serious impact on corrosion than just one species alone. One such example could be the combined effect of sulphate reducing bacteria and iron reducing bacteria. Such possibilities have been mentioned and discussed elsewhere[6]. All such possibilities will add more into the complexity of MID of reinforced concrete structures.

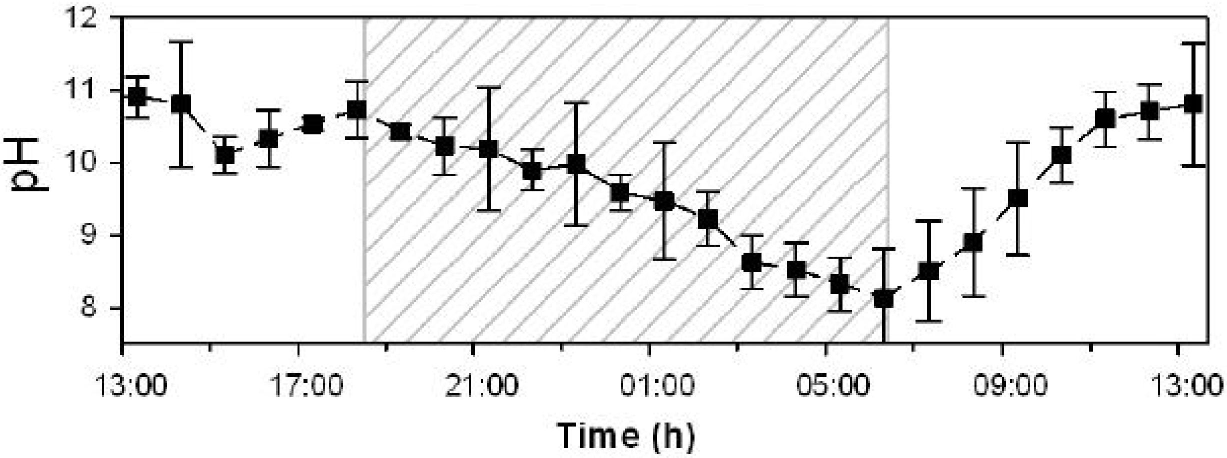
Figure 7: Dissolved oxygen pattern changes for *Pleurochrisis carterae* grown outdoor in a 1 m^2 raceway pond[24]. The oxygen cycle can help the algae establish differential aeration cells and thus enhance corrosion.



Yet another scenario by which algae can play a role in the damage to concrete could be due to the fact that algae are capable of excreting organic acids [25,26,27] . Corrosive effect of organic acids on concretes, especially Portland cement concrete is a known effect[28]. Briefly, when portlandite and hydrated products in ordinary Portland cement are dissolved and form the corresponding calcium salt of the attacking acid, it is the solubility of this calcium salt of the acid that primarily controls the rate of corrosion and not the strength of the acid[29]. There are generally two models of acid attack and deterioration in hydrated Portland cement concrete; one can typically be seen in the acid attack by hydrochloric, nitric and acetic acid whereas the second mechanism can be observed by acids such sulphuric, phosphoric and oxalic acids. More details about such mechanisms have been given elsewhere[30].

However, algae are also capable of producing alkaline environments due to CO_2 uptake during photosynthesis where the pH –especially for the concrete- could be repairing and useful. Figure 8 shows how pH of the medium containing algae can fluctuate between alkaline values.

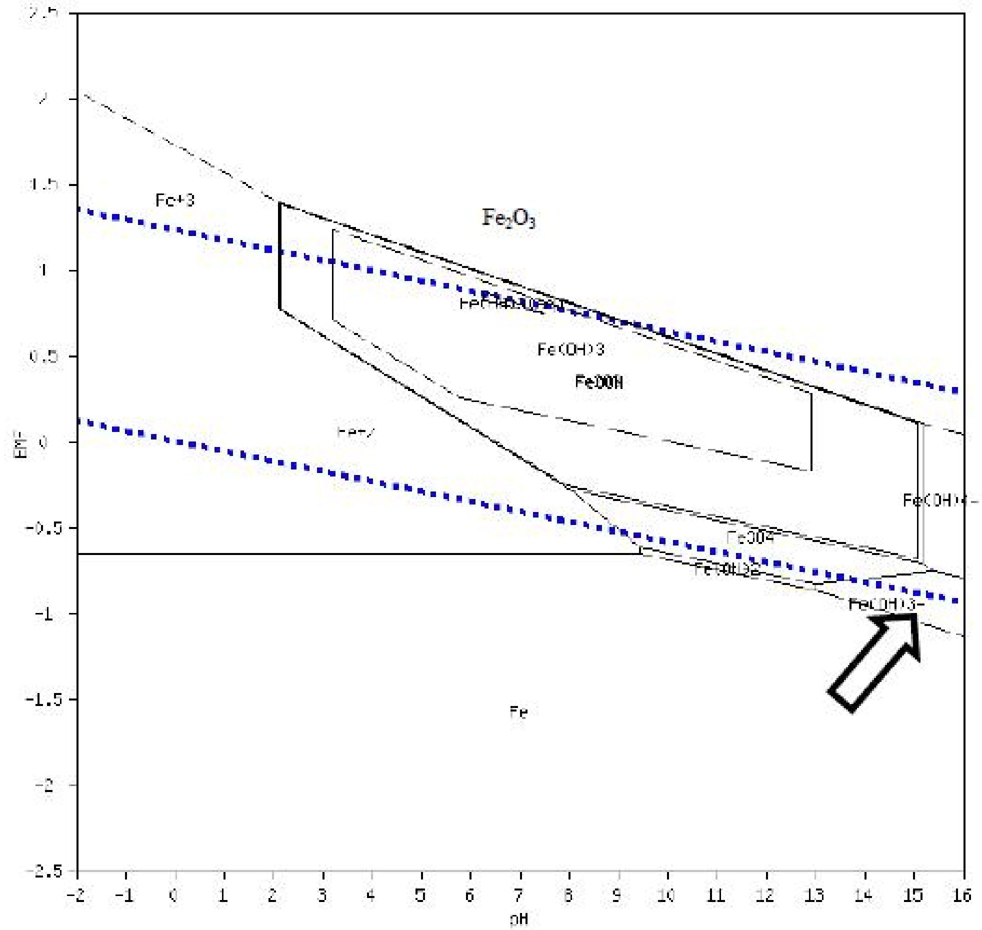
Figure 8: Diurnal pH change pattern over a 24 hour cycle for *Pleurochrisis carterae* grown in a 1 m^2 raceway pond outdoor [23].



As seen from the figure, the algae over a 24-hour cycle shows a pH fluctuating pattern whereas its lowest value can be as low as pH= 8. This pH is not aggressive to concrete and surely, when it comes to carbon steel, such pH conditions can generate conditions that will favor the passivation of the steel, and thus reducing the likelihood of corrosion.

However , one of the tools that can assist us in determining the thermodynamic likelihood of corrosion is the so-called Pourbaix diagrams. These diagrams, based on the potential of the system and the pH, show if a certain reaction can be thermodynamically favourable under certain temperature and electrochemical conditions. Figure 9 shows one example of such diagrams for iron in water. As can be seen, under favourable potential conditions for a system of Fe-H_2O at 25ºC and having 10^{-6} M dissolved Fe, too alkaline conditions for carbon steel can also be corrosive, causing caustic embrittlement.

Figure 9: Pourbaix Diagrma for iron-water at 25ºC[31]. The area designated by arrow shows where caustic corrosion of steel can be expected. The upper and lower dashed lines show the thermodynamic boundaries for water stability.



It is under such conditions that although the presence of algae may increase the safety margin for the concrete due to increased pH, it could also have a potential danger for the steel reinforcement- especially if the steel is exposed due to other erosion-corrosion mechanisms- in terms of inducing caustic corrosion.

Conclusions

In this review, we have shown that:

- To characterise the deterioration/corrosion of reinforced concrete in the presence of biological agents such as algae, it is more useful and practical to talk about two sets of processes that although they may be related to each other, it is prudent to consider them seperately from each other when looking at defining the failure of reinforced concrete structures. These processes are microbiologically influenced corrosion (MIC) of the steel reinforcement and the microbiologically influenced deterioration (MID) of the concrete.
- Due to the complexity involved in characterizing MIC?MID of reinforced concrete structures, a better understanding of some of the basic corrosion/deterioration is necessary.
- Boring of micro-organisms (including algae) on limestones and their related mechanisms are a known phenomena [32,33] . With regards to the role of algae in enhancing the failure of reinforced

concrete structures, four main corrosion/deterioration mechanisms that may be operative on these structures could be as follows:

  - Absorption of some chemicals necessary for the algae from within the cement paste of the concrete: this mechanism can finally result in drying out the concrete and developing cracks as a result of formation of internal cavities and voids.
  - Biofilm formation that will increase the likelihood of attracting more micro-/macro-organisms that can either deteriorate the concrete itself or the reinforcement steel inside , or both. An example is the development of an environment favorable to the acid-producing sulphur oxidising bacteria which through generating very acidic conditions are capable of doing harm to both metallic and non-metallic phases of the reinforced concrete.
  - Development of electrochemical cells such as differential aeration cells due to photosynthetic oxygen production and respiratory oxygen consumption by algae. In this way, it is likely that spots of varying oxygen partial pressures will be created, thus facilitating the corrosion of the steel inside.
  - Production of acids that can be detrimental to the mechanical integrity of both concrete and steel reinforcement.
  - Production of alkaline conditions that upon varying and fluctuating due to the chemistry of the system, can protect the concrete but do damage to the steel phase via mechanisms such as caustic embrittlement.

- While the above mechanisms may happen individually, we hypothesize that it is quite possible for all to happen, though by different rates, thus making the picture even more blurred. For example, it is possible that via biofilm formation, some acid producing bacteria will be able to create growth conditions favorable for the algae to produce more organic acid and thus making the environment quite acidic and thus detrimental to concrete. This is certainly a matter that will require further research and study in future works.

On-going Work

Recently, at the Department of Civil Engineering, Curtin University in collaboration with the Algae R&D Centre, School of Biological Sciences and Biotechnology, Murdoch University, there is a research project going on that focuses on MID of reinforced concrete and geopolymers under the effect of algae and some corrosion-related bacteria. The results of this research will show how in the presence of such micro-organisms the processes of deterioration and corrosion will be affected.

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