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Evaluation of Bacterial Concrete Corrosion Resistance in Marine Settings: A Morphological Analysis Perspective

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Abstract

Concrete is widely used as a structural material worldwide. However, cracks are inevitable and represent one of its inherent weaknesses. These cracks allow water and salts to seep through, initiating corrosion and reducing the lifespan of concrete structures. The high cost of repair and maintenance, coupled with the difficulty of identifying cracks in large, complex structures, underscored the need for a self-repairing material. Bacterial concrete emerges as a promising solution capable of remediating cracks and fissures in concrete. This technique is appealing because the mineral precipitation induced, specifically calcium carbonate, resulting from bacterial activity, is both pollution-free and natural. This paper explores the repair of artificial cracks in concrete structures using *Bacillus subtilis* bacteria and investigates the corrosion resistance of bacterial concrete under marine conditions through microscopic analysis. A comparison with conventional concrete is also conducted. The mix design is based on IS-10262-2019 standards, initially prepared for moderate conditions. However, testing under extreme conditions will provide a better understanding of which type of concrete, bacterial or conventional, better resists corrosion.

Keywords: Marine Environments, Repair of cracks, Bacterial Concrete, Corrosion resistance of concrete, *Bacillus subtilis*, SEM analysis and Durability

1. Introduction

1.1 General

Concrete, as a structural material, received extensive use all over the world during the 20th and 21st centuries. The rapid development of ready-mixed concrete is one of the important signs of concrete technological progress and overall quality improvement. The most prominent problem associated with concrete is its higher probability of cracking caused by non-load factors due to its low tensile strength, such as shrinkage cracks, thermal cracks, and chemical reaction cracks. Cracking increases the probability of aggressive substances ingress into the concrete, endangering the durability of the material. Usually, cracks are mended by hand, which is unsatisfactory because cracks are often hard to detect and the maintenance and repair cost is high. Accordingly, self-healing of cracked concrete would be highly beneficial, and research on self-healing concrete has been widely carried out [1].

Structures built in high water environments, such as underground basements and marine structures, are particularly vulnerable to steel reinforcement corrosion. Motorway bridges are also vulnerable because salts used to deice the roads penetrate into the cracks in the structures and can accelerate the corrosion of steel reinforcement. In many civil engineering structures, tensile forces can lead to cracks, and these can occur relatively soon after the structure is built. Repair of conventional concrete structures usually involves applying concrete mortar, which is bonded to the damaged surface. Sometimes, the mortar needs to be keyed into the existing structure with metal pins to ensure that it does not fall away. Repairs can be particularly time-consuming and expensive because it is often very difficult to gain access to the structure to make repairs, especially if they are underground or at a great height.

1.2 Bacterial concrete

Bacterial concrete addresses the problem of cracks through its self-healing properties after hardening [2]. Concrete is one of the most widely used construction materials due to its high compressive strength, cost-effectiveness, and ease of use. High-strength concrete is prone to cracking, which affects its durability and strength [3]. The self-healing process is achieved through the bacterial reactions in the concrete. It is also observed that cracks ranging between

0.05 to 0.1 mm are self-healed over repetitive cycles of dry and wet climates. The cracks in the concrete heal themselves by reacting with the liquids that flow through them, causing the concrete to expand and fill the cracks. It helps in filling smaller cracks in the range mentioned above. However, construction with big cracks is not healable with bacterial concrete. Various methods have been developed to create minerals in concrete through bacterial reactions [4]. The bacterial reactions in the concrete are achieved through the bacterial acids mixed with the concrete. The lifespan of these bacterial acids is around 200 years, under dry conditions. These bacteria act as catalysts in the crack-healing process. Subtypes of bacillus bacteria such as sphaericus, subtilis, cohnii, and balodurans are widely used in bacterial concrete [5].

In the present study *Bacillus subtilis* is used for preparing bacterial concrete. *Bacillus subtilis* also known as the hay bacillus or grass *bacillus*, is found in soil and the gastrointestinal tract of humans. A member of the genus *Bacillus*, *Bacillus subtilis* is rod-shaped and forms tough, productive endospores, allowing it to tolerate extreme environmental conditions. It is considered the best-studied gram-positive bacterium and a model organism for studying bacterial chromosome replication and cell differentiation. Self-healing of cracks in concrete would contribute to a longer service life of concrete structures and would make the material not only more durable but also more sustainable [6]. *Bacillus subtilis* repairing these cracks with the production of calcium carbonate crystals that block cracks and pores would be an immense solution. This state-of-the-art facility offers a more cost-effective, eco-friendly, and efficient solution for cracks in concrete. Since concrete is highly alkaline, a bacterium that can endure alkalinity would be the best choice. *Bacillus subtilis* is an ideal bacterial species for self-healing concrete. Bacterial concrete claims to have higher tensile strength, compressive strength, high water permeability, and durability compared to conventional concrete.

1.4 Biological self-healing process

Buildings constructed with concrete are experiencing cracks due to climatic conditions, with some cracks reaching up to 2mm wide [9].Cracks of this size are deemed acceptable according to industrial standards. However, smaller cracks of about 0.2mm are prevalent in normal concrete buildings, many of which eventually widen to 2mm. Self-healing concrete is specifically designed to address cracks of 0.2mm in size. It utilizes bacteria that react with fresh air or moisture to heal the cracks, resulting in improved durability compared to conventional concrete. The durability of self-healing concrete is much better than the normal ones [7]. This healing process is based on bio-calcification, wherein limestone is formed through a reaction with moisture. The efficiency of this method can be evaluated using X-ray diffraction and SEM analysis methods. The bacteria mixed with the concrete remain inactive until cracks appear, at which point they are exposed to the environment and begin to feed on oxygen, facilitating the conversion of calcium lactate mixed in the cement into limestone. As the bacteria absorb oxygen from the atmosphere, the calcium lactate is transformed into limestone, effectively filling the cracks [8](Eq. 1-2).

$$CO_2 + Ca(0H)_2 \rightarrow CaCO_3 + H_2O \text{---------- Eq. (1)}$$

$$CaC_6H_{10}O_6 + 6O_2 \rightarrow CaCO_3 + 5CO_2 + 5H_2O \text{---------- Eq. (2)}$$

1.3 SEM analysis

A scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (SEM-EDX) is an important supplement to the optical microscope when examining new, old, and deteriorated concrete. In quality assurance of concrete, scanning electron microscopy provides important information about degree of hydration of cement, formation and distribution of hydration products, adhesion to aggregates and homogeneity of cement paste.

In relation to forensic investigations on deteriorated concrete, scanning electron microscopy may add valuable data about the cause of deterioration. SEM-EDX analysis typically supplies information on primary and secondary mineral phases in paste, pores, cracks, and micro cavities, morphology of phases, phase assemblage analysis, source and deposition area for the mineral phases, identity of tiny micron-sized mineral phases not visible in the optical microscope, chemical composition of mineral phases and chemical zoning or variation through crystals and throughout the entire material [12].

2. Bacterial Concrete Materials

A grade 43 Portland cement is used in this experiment, which is widely utilized in various other studies. The properties of the Portland cement are listed in Table-2. The mixture primarily consists of cement, coarse aggregate, fine aggregate, and water. The coarse aggregates are obtained by crushing granite stones and fine aggregate is sourced from a river. The properties of fine and coarse aggregates are listed in Table-3. Potable water available in the area is used. In this study, Bacillus subtilis is considered for mixing with the concrete to produce bacterial concrete. Different proportions of bacterial solution are used in the mix preparation. The entire set of materials used in this study is shown in Table-1.

Table-1.Material Used in the bacterial concrete

Materials	Specifications
Cement	Ordinary Portland 43-grade cement
Fine aggregate	The river sand
Coarse aggregate	6mm, 12mm, and 20mm size
Water	Potable water
Bacteria	Bacillus subtilis
Calcium lactate	$C_6H_{10}CaO_6$ (Used as nutrient broth along with the bacteria)

Table-2. Properties of Portland cement

Property	Results	Requirement
Fineness		
Sieve test	2%	
Blaine	285m^2/kg	
Normal Consistency	31.0%	
Specific Gravity	3.01	
Initial setting time	95 minutes	> 30 minutes
Final setting time	284 minutes	< 600 minutes
Compressive strength		
3 days	28 N/mm^2	27 Nmm^2(Min)
7 days	41 N/mm^2	37 N/mm^2(Min)

28 days	56 N/mm^2	53 N/mm^2(Min)
Soundness	2mm	Only < 10mm

Table-3. Properties of fine and coarse aggregate

Property	Fine aggregate	Coarse aggregate
Specific Gravity	2.67	2.64
% of maximum bulking	29.5%	-
Bulk density	-	1.384g/cc
Water absorption	3	-
Sieve analysis	Zone-II	20 mm
Porosity	24.2%	-
Void ratio	0.319	0.581

2.1 Preparation of bacterial solution

Bacillus subtilis bacteria should be cultured before being mixed into the concrete. To prepare the culture, add 1.5 grams of beef extract, 2.5 grams of peptone, and 2.5 grams of NaCl to 500ml of distilled water in a conical flask. Seal the mouth of the conical flask with cotton and cover it with silver foil. An autoclave is used to sterilize the nutrient broth solution for 20 minutes at 121°C with 15 lbs pressure. Water is filled in the autoclave up to level 1. This process removes contaminants from the solution, resulting in an orange-coloured solution. Subsequently, the flask is opened and exposed to laminar airflow, and a pinch of bacteria is added to the solution [10].The flask is then placed in an orbital shaker and maintained at 125 rpm at a temperature of 37°C. As the bacteria grow, the color of the solution changes to turbid yellow, indicating the growth of Bacillus subtilis (Figure-1).

Figure-1 Making of bacterial solution

3. Mix design and proportion

Mix design can be defined as the process of selecting suitable ingredients for concrete and determining their relative amounts to produce concrete of the required strength, durability, and workability as economically as possible. The mix proportioning is carried out to achieve specified characteristics at a specified age, workability of fresh concrete, and durability requirements. The mix design for conventional concrete was carried out according to IS 10262:2019.

The concrete compositions, as outlined in Table-4, are initially mixed while wet for thirty seconds. After this, the bacterial solution is introduced into the mixture. Thirty seconds later, water is added. The substance is then equalized with additional water after 15 minutes of mixing. Following one minute of mixing, all components are transferred into a pan. After thorough mixing for three minutes and allowing the mixture to form a mould, the concrete is tested and subsequently employed in the building process a few days later. The mixing design adheres to IS: 10262:2009 requirements. The concrete grade selected is M30, with a maximum aggregate size of 20mm and sand grade of Zone-II. The proportions for the M30 grade concrete are detailed in Table-4. Based on various mixing calculations, including test data of the materials, target strength, water and cement content, and proportions based on coarse and fine aggregate, the material mixing proportions are specified in Table-4

Table-4. Sample concrete materials

Water	Cement	Fine	Coarse	Super plasticizer	Bacteria
202.74	482.71kg	600 kg	1064.5 kg	1.5% of weight of cement	30 ml Bacillus subtilis solution (Optimum amount)

To determine the optimum amount of bacterial solution, three cubes were cast for each proportion, with 15 ml, 30 ml, and 45 ml of bacterial solution added to the concrete mix. From Table-5, it can be found that the optimum concentration of bacteria for maximum strength gain is 30 ml. Up to a concentration of 30 ml, the strength of concrete increases [11]. This increase is attributed to the increased filling of pores as the concentration rises, with the compressive strength peaking at a concentration of 30 ml. However, beyond this concentration, the strength begins to decrease. This decline may be due to the higher concentration of bacterial cells causing disruption in the concrete matrix, resulting in a reduction in compressive strength. The table also demonstrates that the performance of bacterial concrete in terms of compressive strength is significantly better than that of normal concrete.

Table -5 Compressive strength of concrete

Days	Normal concrete compressive strength (N/mm^2)	Bacterial concrete samples	Bterial concrete Compressive strength (N/mm^2)
7 days	20.65	A (15ml)	27.23
		B (30ml)	28.41
		C (45ml)	27.41
28 days	35.02	A (15ml)	40.79
		B (30ml)	43.22
		C (45ml)	40.63

4. Test procedures

This section describes the methodology used to achieve the objectives of the work. Details of the methods adopted in preparing the test specimens and the different test procedures are discussed. The methods employed in preparing the test specimens, including casting and curing, are also described. Size of beam mould is 100cm X 20cm X 25cm and of slab mould is 50cm X 40cm X

15cm. There are four beams made of normal concrete and four made of bacterial concrete, along with three slabs of each type (Figure -2). The casted beams and slabs are removed from the mould within 24 hours. Specimens are kept in sea water for 28 days, 90 days, 120 days and 365 days

Figure-2 Specimen preparation

5. Results and discussions

5.1 Corrosion of reinforcement

All specimens were retrieved from seawater after the designated time. Figure 3(a) depicts the normal concrete beams before immersion in seawater, while Figure 3(b) illustrates them after removal from the seawater. Figures (c) and depicts the corroded rebars in normal concrete after 365 days of immersion in seawater. Additionally, Figures 4(a) and (b) illustrate the bacterial concrete before and after immersion in seawater. One side of the beam cover is removed to inspect the reinforcement for signs of corrosion. It is evident from Figure 4(c) that the rebar in bacterial concrete shows no signs of corrosion.

(a) (b) (c)

Figure -3 Normal concrete beams before and after 365 days of immersion in sea water

(a) **(b)** **(c)**

Figure-4.Bacterial concrete beams before and after 365 days of immersion in sea water

Additionally, Figures 5 and 6 show normal and bacterial concrete slabs before and after immersion in seawater, as well as the corrosion rate in both. Here also bacterial concrete slab shows very less corrosion.

(a) **(b)** **(c)**

Figure-5 Bacterial concrete slab before and after 365 days of immersion in sea water

(a) **(b)** **(c)**

Figure-6 Bacterial concrete slab before and after 365 days of immersion in sea water

5.2 Loading tests on UTM

Table 6 illustrates the ultimate load and breaking load values of normal and bacterial concrete beam specimens tested in the Universal Testing Machine (UTM). It is evident from the results that both ultimate and breaking loads are higher for bacterial concrete than for normal concrete. Similarly, in the case of slab specimens, as illustrated in Table 7, higher values are observed for bacterial concrete in terms of ultimate and breaking loads.

Table -6 UTM test results for beam specimens.

Number of days of curing	Normal concrete beam (kN)		Bacterial concrete beam (kN)	
	Ultimate load	Breaking load	Ultimate load	Breaking load
28 days	74.05	108.43	95.03	121.39
90 days	60.21	80.64	70.65	102.08
180 days	53.97	67.04	59.29	82.90
365 days	32.52	50.31	42.34	72.61

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Table -7 UTM test results for slab specimens.

Number of days of curing	Normal concrete slab (kN)		Bacterial concrete slab (kN)	
	Ultimate load	Breaking load	Ultimate load	Breaking load
28 days	69.66	88.63	104.04	124.25
90 days	55.55	67.18	92.51	106.27
180 days	49.88	56.42	86.56	94.32
365 days	34.01	46.18	64.02	72.72

5.3 SEM analysis-Morphological Study

For the Scanning Electron Microscopy also known as SEM Analysis, Samples were taken from both bacterial and non-bacterial beams, extracted from the crack healing zone and reinforcement zone and observations were conducted regarding minerals, pores, and compounds. Figure 7 illustrates the crack healing zone of bacterial concrete. This figure demonstrates that the artificial crack created for SEM analysis was filled with calcium carbonate precipitates resulting from bacterial reactions, leading to eventual healing of the crack. Figure 8 provides a closer view of the $CaCO_3$ crystals present in the healing zone.

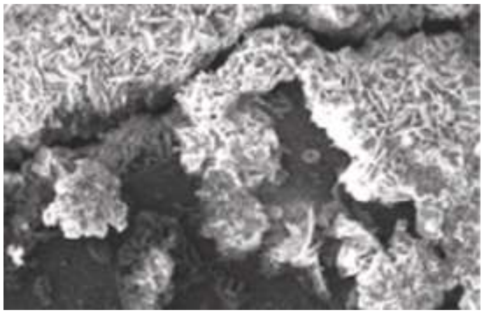


Figure 7 Crack healing zone of bacterial concrete

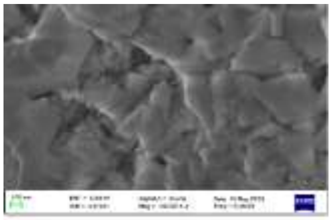


Figure 8 Calcium carbonate precipitations at crack healing zone

Figure 9 illustrates the reinforcement zone of normal concrete beam that underwent continuous immersion in seawater for 365 days. The annotations in the figure identify the reinforcement area (a), an iron oxide layer (b-b'), fragments of rust (c), and iron oxide crystals (d). The figure clearly demonstrates that the reinforcement zone experienced corrosion attributed to the infiltration of saline water and other aggressive agents through the pores in normal concrete. However, the bacterial concrete specimen depicted in Figure 10 reveals reinforcement zone where an increased presence of calcite and a reduction in pores and iron oxide. This phenomenon can be attributed to the formation of calcium carbonate deposits within the pores, a result of the interaction between external agents like saline water and the bacteria present in concrete.

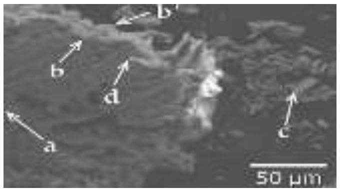


Figure 9 Reinforcement zone of a normal concrete beam

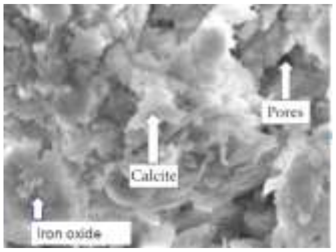
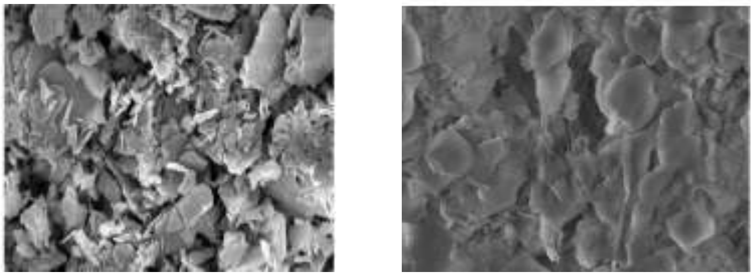


Figure 10 Reinforcement zone of bacterial concrete

In Figure 12(a), the sharp-edged crystals depicted are rust particles observed in normal concrete, whereas Figure 12(b) lacks such crystals, rich in lime and the minerals are tightly packed . This suggests that bacterial concrete has fewer pores due to the deposition of calcium carbonate and hence lesser corrosion and higher durability.



(a) Normal concrete **(b) Bacterial concrete**

Figure 12 Crystals of rust and lime in normal and bcterial concrete

Table -8 Comparison between the atomic percentage of the important elements and compounds present in bacterial and normal concrete

Elements or compounds	Atom percentage in normal concrete	Atom percentage in bacterial concrete
Carbon	20.6	13.6
Chlorides	22.92	0.06
Iron oxide	10.9	3.3
Oxygen	10.8	18.3
Aluminium oxide	3.42	0.25
Magnesium sulphate	11.47	0.8
Sulphur dioxide	7.43	0.1
Calcium carbonate	0.33	46.91

Table 9 displays the atomic percentages of the elements and compounds found in bacterial and normal concrete. Carbon content is notably higher in normal concrete, indicating a greater likelihood of carbonation occurring in normal concrete. Carbonation diminishes the pH of concrete, contributing to diminished durability. Additionally, the presence of Sodium carbonate in concrete can prompt significant expansion, potentially resulting in complete disruption and disintegration of the concrete in severe cases.

When considering concrete durability, chloride attack emerges as the most significant threat, accounting for nearly 40% of concrete structure failures. In the presence of oxygen and water, chloride attack initiates corrosion in steel reinforcements, significantly compromising the structure's strength. While chlorides have minimal impact on hardened concrete, they elevate the risk of reinforcement corrosion. Corrosion of the reinforcement begins once the chloride ion concentration at the steel surpasses the critical 'threshold level.' For normal Portland cement concrete, with cement content ranging between 254 and 446 kg/m3, estimated chloride threshold values typically fall between 1.6% and 3.6% [13]. In the case of normal concrete, from Table 7, the chloride content registers at 22.92% posing substantial risk. Conversely, bacterial concrete exhibits a chloride content of only 0.06%, indicating its exceptional resistance to chloride attack, particularly in marine environments. Thus bacterial concrete exhibits superior durability compared to normal concrete, as the percentage of chlorides is higher in normal concrete than in bacterial concrete.

The iron oxide content in concrete products is typically restricted to 3 to 4% to prevent a reduction in the mechanical strength of the product [14]. In Table 7, the iron oxide content in normal concrete is 10.9%, whereas in bacterial concrete, it falls significantly within the acceptable range. Atomic oxygen is a part of many construction materials, including concrete, and without oxygen, this strong material would lose most of its binding properties, and would simply turn to different chemical elements. In the bacterial concrete, from Table 7, oxygen is more than that in normal concrete. This indicates that bacterial concrete is stronger than normal concrete.

Excessive aluminum oxide in cement can result in decreased strength and durability of the concrete. This occurs due to the excessive presence of aluminum oxide, which can prompt the formation of a mineral known as *ettringite,* leading to expansion and cracking within the concrete. Such expansion undermines the durability and structural integrity of the concrete. Moreover, an excess of aluminum oxide can impact the setting time and workability of the cement, making it more challenging to handle. Table 7 illustrates that bacterial concrete surpasses normal concrete, evident in its lower aluminum percentage.

The process of concrete sulfate attack is complex, involving both physical salt attack from salt crystallization and chemical sulfate attack by sulfates present in soil, groundwater, or seawater. Sulfate attack can result in expansion, cracking, strength loss, and disintegration of the concrete. This phenomenon is particularly detrimental to reinforced structures and operates through two mechanisms, yielding high-volume products such as ettringite, gypsum, Thaumasite, and salt crystals. The expansion caused by these products induces internal tensile stresses within the concrete, leading to spalling, cracking, or disintegration. Magnesium sulfate attack further exacerbates concrete degradation by lowering pH levels, hastening the formation of gypsum, and intensifying deterioration. In standard concrete, sulfate attack is more pronounced, especially in environments exposed to seawater. The porous nature of concrete renders it highly susceptible to magnesium sulfate attack, resulting in accelerated degradation. Conversely, from Table 7, bacterial concrete exhibits significantly lower levels of magnesium sulfate. Consequently, bacterial concrete demonstrates greater resistance to sulfate attack compared to standard concrete, making it a safer option for marine applications.

Concrete's pores are filled with a highly alkaline solution, boasting a pH between 12.6 and 13.8, contingent upon moisture levels. This solution, rich in alkalinity, stems from by-products formed during hydration reactions in the cement clinker. Maintaining a high pH within concrete pores is pivotal for resisting steel corrosion. Corrosion induced by sulfur dioxide in reinforced concrete manifests in three forms: chemical corrosion, deteriorating the concrete itself, and electrochemical and electrolytic corrosion targeting reinforcing carbon steel [15]. Chemical corrosion of concrete is propelled by reactions and transformations of calcium silicates ($CaO{\cdot}SiO_2$) and calcium oxides (CaO), yielding new products with volumes far surpassing the initial constituents, thus promoting concrete fragmentation. Electrochemical corrosion and deposit corrosion occur via electrolyte penetration (SO_2, O_2, and water) into the carbon steel bar through faults, fissures, and porosities within the reinforced concrete structure. The expansion of corrosion product volumes (FeO, $Fe(OH)_2$, Fe_3O_4, and FeOOH) from steel bars further contributes to concrete fragmentation. Notably, the sulfur content in concrete should not exceed 2.75%. From Table 7, it's evident that bacterial concrete proves effective in marine conditions due to its resistance to sulfur attack, attributed to its lower sulfur content percentage.

CaCO3, a natural material, boasts finer particle sizes compared to cement particles, enhancing the particle packing of concrete and providing a spacer effect [16]. Concrete containing CaCO3 replacement demonstrates a higher slump, thereby improving workability. Moreover, CaCO3 aids in increasing early strength by accelerating hydration rates, resulting in quicker concrete hardening. While concrete with CaCO3 addition may exhibit lower strength at matured ages compared to concrete without CaCO3, it typically still meets target strength requirements.

Calcium carbonate not only fills voids between cement grains but also accelerates the hydration process, influencing workability, mechanical properties, and durability through dilution, nucleation, and chemical effects. From Table 7, in bacterial concrete, the CaCO3 content exceeds that of normal concrete due to bacterial reactions with external aggressive agents that infiltrate concrete through its pores. Consequently, bacterial concrete presents a sustainable solution for infrastructure in marine conditions.

6.Conclusion

Saturation of concrete with seawater results in a solution mostly consisting of magnesium sulphate and sodium chloride. Any damage to the concrete typically arises from poor construction practices rather than the direct effects of seawater itself, often resulting from cycles of freezing and thawing or repeated wetting and drying. Magnesium sulfate has the potential to corrode most, if not all, components of hardened Portland cement paste, particularly the aluminate component. Chlorides can accelerate the corrosion of steel, while alkalies may contribute to alkali-aggregate reactions. To mitigate these risks, concrete exposed to seawater should be composed of cement with controlled aluminate content and non-reactive aggregates. Additionally, embedded steel should be adequately covered by low-permeability concrete, and construction should adhere to sound practices.

Cracks are inevitable in concrete; however, bacterial concrete possesses crack healing or self-healing capabilities, readily repairing cracks through lime precipitation. In contrast, normal concrete is susceptible to rusting due to iron oxidation, while bacterial concrete mitigates reinforcement corrosion by significantly reducing porosity through lime deposits within the pores. Bacterial concrete exhibits greater bending stress compared to normal concrete and boasts a substantially higher load-carrying capacity, extending the service life of structures, particularly in marine conditions. Given that cracks and corrosion are primary durability concerns in concrete structures, bacterial concrete emerges as a promising solution. It stands as the most suitable natural, eco-friendly, organic material for combating excessive corrosion in marine environments compared to other methods and materials

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