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Current understanding and Future Approaches for Controlling Microbially Influenced Concrete Corrosion: A Review

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Abstract

The microbes colonize the concrete surface and its pores, capillaries and micro-cracks and cause damage through biodeterioration. Though the biodeterioration of concrete in sewage pipes is extensively studied, the problems in constructions such as maritime structures, bridges, tanks, pipelines and cooling towers have received lesser attention. In nuclear industry future power plants will be designed for 100 years to make available operation of nuclear power plants for more periods. Therefore, integrity of the concrete structures in nuclear power plants has to be maintained for this long duration specially those exposed to aggressive seawater environment. Nuclear industry is looking at various options including modified concrete with special admixtures and fly ash to achieve this goal. A direction for future approaches like using nanophase modification to get stronger and flexible concrete is given in this paper.

Keywords: Concrete, acidophiles, superplasticizer, fly ash, nanophase modification

1. Introduction

1.1 Microbially Influenced Concrete Corrosion (MICC)

Concrete is basically a mixture of aggregates and paste, and has several hydrated compounds of calcium silicates, calcium aluminates, aluminoferrites and gypsum. The concrete is typically highly alkaline and has a pH in the range of 11 – 13 due to the formation of calcium hydroxide ($CaOH_2$), as a by-product of the hydration of cement [1]. Only extremophiles can survive under this high alkalinity. However, the atmospheric CO_2 is capable of reducing the concrete pH to 9.5 which may favour adhesion of microbes [2]. Earlier investigators assumed that hydrogen sulphide formed either by decomposition of organic material or by sulphate reduction in the environment, get oxidized into sulphuric acid, and cause deterioration of concrete [3].

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The first instance of microbial involvement in the degradation came into light when **Parker (1945**) [4] isolated highly acidophilic sulfur oxidizing bacteria (SOB) *Thiobacillus* sp. from the corroded concrete walls. SOB is considered as the main agents of concrete corrosion.

These chemoautotrophs oxidize various sulfur compounds to produce sulfuric acid, which is responsible for the corrosion and degradation of concrete and this process is known as microbially influenced concrete corrosion (MICC). The sulfuric acid reacts with the free lime, which produces a corroding layer on the concrete surface ($CaSO_4.2H_2O$) that penetrates into the concrete, increasing the degradation due to the large density difference between the reaction products and the concrete [5]. A far more destructive reaction occurs between the newly formed gypsum crystals and calcium aluminate in the concrete. This reaction leads to the production of ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) [6] which further contribute to the degradation of concrete by increasing the internal pressure, leading to the formation of cracks. The cracks in turn provide a larger surface area for corrosion processes and provide additional sites for acid penetration [7].

Many other microbes are also involved in biodeterioration**. Brendt (2001)** [8] described that nitrifying bacteria cause nitric acid biodeterioration. One species of *Nitrosomonas* oxidizes ammonia to nitrite and another species *Nitrobacter* oxidizes nitrite to nitrate and cause deterioration. Nitric acid reacts with calcium hydroxide to produce soluble calcium nitrate. It became evident that mineral acid producing bacteria play an important role in biodeterioration of building material.

Acid producing fungus also plays a big role in concrete biodeterioration**. Gu et al., (1998)** [9] isolated a fungus from concrete samples and identified as a *Fusarium* species and observed both weight loss and release of calcium when concrete was exposed to the isolate. Fungal degradation proceeded more rapidly than *Thiobacillus*-mediated degradation. Fungi dissolved the cement matrix with leaching of structural elements and accumulating them within the fungal biofilm and associated microenvironment. Oxalate-excreting *Aspergillus niger* formed abundant calcium oxalate crystals on the concrete and encrusting fungal hyphae [10]. The influence of microscopic fungi *Coniophora puteana* and *Serpula lacrymans* on Portland cement 450, showed their humidity increased up to 18-25%, the pH decreased from 12 to 5 and bending strength decreased from 5-20% [11].

Microbial metabolites like organic acids, carbon dioxide, mineral acids like sulfuric acid and nitric acid all can cause biodeterioration by reacting with the components of concrete as shown in the equations below [12].

Biogenic Organic acids

$$Ca(OH)_2 + 2\ C_2H_4(OH)COOH + 3\ H_2O \rightarrow Ca[C_2H_4(OH)COO]_2.5\ H_2O \qquad [1]$$

lactic acid calcium lactate

$$Ca(OH)_2 + 2\ CH_3COOH \rightarrow Ca(CH_3COO)_2.H_2O + H_2O \qquad [2]$$

acetic acid calcium acetate

Biogenic Carbon dioxide

$$Ca(OH)_2 + 2\ CO_2 \rightarrow Ca(HCO_3)_2 \qquad [3]$$

$$CaCO3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2 \qquad [4]$$

Biogenic Nitric acid

$2\ NH_4^+ + 3\ O_2$ Nitrosomonas $\rightarrow 2\ NO_2^- + 2\ H_2O + 4\ H^+$ [5]

$2\ NO_2^- + O_2$ Nitrobacter $\rightarrow 2\ NO_3^-$ [6]

$Ca(OH)_2 + 2\ HNO_3 \rightarrow Ca(NO_3)_2 + 2\ H_2O$ [7]

Biogenic Hydrogen Sulfide and sulfuric acid

$SO_4^{2-} + 2\ H^+ + 4\ H_2$ SRB $\rightarrow H_2S + 4\ H_2O$ [8]

SRB – Sulfate Reducing Bacteria

$H_2S + 2\ O_2$ SOB $\rightarrow H_2SO_4$ [9]

SOB – Sulfur Oxidizing Bacteria

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2\ H_2O$ (gypsum) [10]

$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O + 3(CaSO_4 \cdot 2\ H_2O) + H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ [11]

(Gypsum) (Ettringite)

2. MICC in various industries

Maximum research on biodeterioration of concrete is confined to the problems in sewers till end of 1995. **Gu et al. (1998)** [9] showed aerobic microbes like fungi in atmosphere can cause biodeterioration of concrete buildings, in humid environments. Following these **Berndt et al. (2001)** [8] also reported presence of nitrifying bacteria on the exteriors of bridges causing nitric acid degradation. However the concrete biodeterioration problems in constructions such as maritime structures, bridges, tanks, pipelines, cooling towers has not received systematic attention. However, different modified concrete were randomly compared to see the resistance to attack in many fields. The concrete structures in nuclear power plants are designed for a life span of 30-40 years but with the experience gained so far future power plants will be designed for 100 years to make available operation of nuclear power plants for more periods. Therefore, integrity of the concrete structures in nuclear power plants has to be maintained for this long duration specially those exposed to marine environment.

2.1. MICC of sewage system

In the early 1980s, rapid deterioration of new sewer systems in Hamburg, Germany [13] and in US cities [14 and 15] renewed interest in the microbial processes involved in concrete pipe degradation. The deterioration of concrete in sewers is a complex process involving several sulfur compounds and several species of microorganisms. The crown of the pipes in the sewage collection system is usually covered by condensate which together with adequate supplies of carbon dioxide, oxygen and hydrogen sulfide allows the existence of a diverse population of microbes inducing biodeterioration [16]. **Olmstead and Hamlin (1900)** [17] first reported the rapid corrosion of sewage transport pipelines built from concrete. Parker along with his coworkers established role of microbes by isolating a highly acidophilic *Thiobacillus* (*Thiobacillus concretivorus* = *Thiobacillus thiooxidans*) from corroded sewers [18]. **Kadota and Ishida (1972)**

[19] observed ‘Hydrogen sulphide corrosion’ in warm climates due to high content of sulphur compounds in detergents and an increase in the protein content of the sewage that leads to higher production of volatile sulphur compounds by amino acid degradation. Many workers have observed extensive microbially induced concrete corrosion (MICC) in sewers, in both pipes and at pipe line junctions [20 and 21].

Fig. 1 shows the graphical representations of MICC in sewage collection systems. First step is the conversion of sulfate in sewage into hydrogen sulfide by sulfate reducing bacteria (SRB). SRB are heterotrophic bacteria found in any environmental sample and the energy of the reduction of sulfate is supplied by the oxidation of organic compounds or H_2 [22]. The H_2S produced by SRB is the dominant species in the slightly acidic sewage (pH 5-6). This H_2S will partition into the headspace of the sewer. Then it is re-partitioned into the condensate layer on the concrete surface due to high pH initially. In the presence of oxygen the sulfide species will react to form partially oxidized sulfur species such as thiosulfate, elemental sulfur and polysulfate species. Then the sulfur-oxidizing bacteria convert these reduced sulfur compounds to sulfuric acid. However these SOBs cannot survive on fresh concrete with elevated pH. CO_2 and H_2S present in the headspace can reduce the pH of the concrete surface [23]. Once the pH reduces to ~ 9 with sufficient nutrients, moisture and oxygen many species of *Thiobacillus* can colonize the surface (Fig 2) [24]. Five species of *Thiobacillus* play an important role in concrete corrosion; T. *thioparus*, T. *novellas*, T. *neopolitanus*, T. *intermedius* and T. *thiooxidans*. The first four species are neutrophilic sulfur-oxidizing microorganisms (NSOM) and last one is an acidophilic sulfur-oxidizing microbe (ASOM). NSOMs colonize during pH 9 and they produce acidic products that convert lot of sulfide to elemental sulfur and polythionic acids. Then the pH drops to 4-5 and ASOM colonize and oxidize sulfur and polythionic acids to sulfuric acid and sulfur cycle in the sewage system is completed [14, 25]. The final step in the corrosion process is the reaction of biogenic acid with the concrete forming a corroding layer made up of $CaSO_4$ (gypsum). The thickness of this layer expands into the concrete as more and more acid reacts. The formation of ettringite ($3CaO.Al_2O_3.CaSO_4.12H_2O$) during acid reaction is expansive and hence causes internal cracking and pitting providing larger surface area for the chemical reactions and further sites for penetration of acid into the concrete.

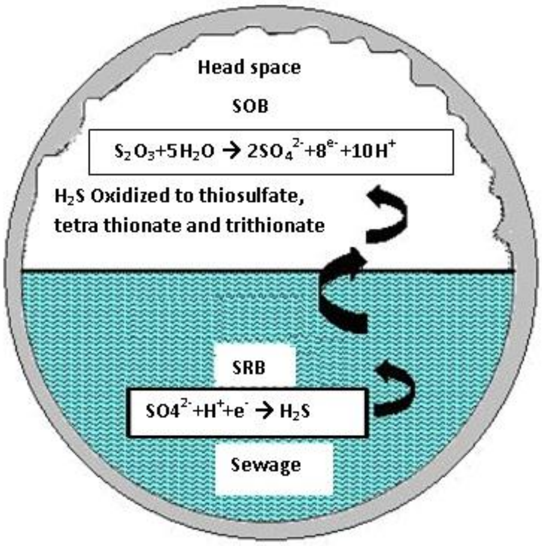

Fig 1: Schematic of S cycle in the sewage pipes

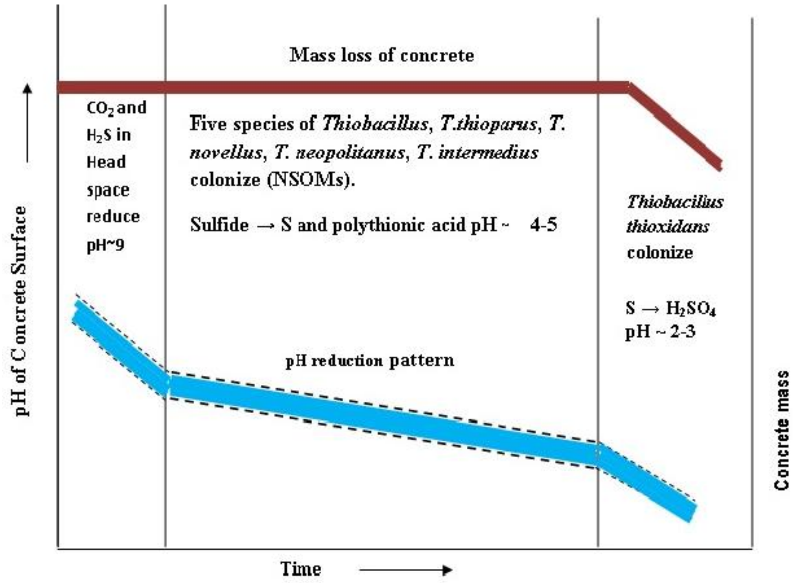

Fig 2: Schematic of pH reduction, biological succession of NSOM and ASOM and concrete mass loss in sewage pipes

Morton et al. (1991) proposed the synergistic effect where the removal of metals from industrial wastes prior to entering the municipal waste water collection system accelerates the corrosion of concrete [26]. The removal of heavy metals from waste water for water quality benefits has resulted in a decreased toxicity to sulphate reducing bacteria (SRB) and has resulted in increased production of sulphide from waste system that results in increased sewer odours and an increase in microbial induced deterioration of concrete structures

Severe concrete corrosion may occur at sulfide concentrations from 2.0 mgS L^{-1} onwards [27]. Sewer pipes are subject to significant sulfide corrosion and restoration of overall damaged sewer systems cost several billions [28]. A recent review describes the chemical and biological technologies for hydrogen sulfide emission control in sewer systems [29]. Past research resulted in number of prevention method, such as injection of air, oxygen, H_2O_2, NaClO, $FeCl_3$ and $FeSO_4$. Biological oxidation of sulfide using nitrate has been explored. All these method are costly, and hence they have suggested some new approaches like a microbial fuel cell to control sulfide emission while BOD is partially removed. Biological control of SRB by phages is also suggested. These authors suggested further study on novel inhibitors such as slow release solid phase oxygen (MgO_2/CaO_2) and formaldehyde for sulfide control.

2.2 MICC of wastewater applications

When majority of studies focused on the deterioration of concrete in sewer systems and pipelines, little detailed research has been conducted into the effect of corrosion on the vital treatment facilities that are processing wastewater [30]. Occurrence of concrete deterioration in these structures have been recorded in a limited fashion in aeration tanks [31], in septic tanks and pumping stations [32] and the underside of concrete slabs and in primary influent channels [33].

Contributory factors to concrete corrosion existing in sewage systems such as high sulfate and dissolved sulfide concentration high temperatures and high biological oxygen demand (BOD) levels, high H_2S gas and low oxygen concentrations, biogenic sulfuric acid production by *Thiobacillus* sp. (SOB), sulfate reduction by sulfate reducing bacteria (SRB), all exist in wastewater treatments plants too. **O'Connell et al. (2010)** [30] in a recent state of art review explains that there still remains a lack of consensus on degradation mechanisms, the performance of various cement types, the role of bacteria in the corrosion process associated with wastewater application. They have outlined a combined approach that considers the interaction between biological and chemical processes like role of SRB and SOB and chemical effects of sulfate and sulfuric acid. **Dubravka et al**. (**2010)** [34] also has presented a review on microbial processes in municipal waste water collection systems, which occur when concrete is exposed to microbacteria and biodegradation favorable environment. They also explained the mechanism of sulfur cycle and methods to test resistance of concrete to microbial corrosion.

2.3. MICC of bridge structures

Nasrazadani and Sudoi (2010) [35] report that in United States hundreds of bridge structures are damaged by MICC. However there is no clear understanding of the extent of damage, how microbes cause damage in these structures and what remedial measures can be adopted. He also anticipated that regions with higher sulfur oxide emissions can cause extensive biodeterioration of concrete bridge structures. **Trejo et al. (2008)** [36] tried to identify the microbes present in the bridge column and tried to correlate the density with the damage of structures. They identified five genera: *Bacillus, Brachybacterium, Flavobacterium, Lysinibacillus* and *Thiomonas*. *Bacillu*s was represented by 17 strains and followed by *Thiomonas* by 7 strains. They identified that many of these bacteria produce acids and the numbers correlated with the damage.

2.4. MICC of concrete structure in cooling water systems

Cooling water systems are either open or closed types and water flow in an open system can be either once through or recirculation [37]. In the open recirculation system, there are many concrete structures in the form of tanks, pillars and reservoirs. Growth of microbial biofilm on concrete structures leading to deterioration of these structures is a serious problem in cooling water systems.

Zherebyateva et al. (1991) [38] describes that cooling towers and hydraulic facilities are susceptible to biodeterioration Open recirculation type of cooling type cooling tower has the greatest potential for fouling and resultant corrosion of concrete and other materials as the cooling tower acts as sink for air borne microbial contaminants. These systems are attractive locations for microbial growth and biofilm formation, since the cooling tower is directly exposed to light and air and it provides optimum condition for microbial growth. The cooling water is highly oxygenated and acts an incubator by providing a temperature range of 27-60^{o}C and a pH of 6-9; these conditions promote biofouling of the concrete surfaces in contact with water in cooling tower.

Concrete in cooling towers used in geothermal power plants is susceptible to microbiologically influenced corrosion (MIC) [39].**Pryfogle (2005)** [40] identified several *Thiobacillus* sp. from geothermal cooling tower basins and cooling effluents from plants in California and Utah. **Brown and Bacon (2009)** [41] did pilot plant experiments in Wairakel geothermal power plants and implicated *Thiobacillus* sp. in attack of concrete culverts carrying cooling water and condensate. **Berndt (2001)** [42] implicated both Sulfur oxidizing *Thiobacillus* sp. and nitrifying bacteria in these environments. The urobacteria present in the environments decompose urea and form ammonia. Bacteria belonging to *Nitrosomonas, Nitrosococcus, Nitrosolobus* genera oxidize this ammonia into nitrous acid and *Nitrobacter* and *Nitrococcus* oxidize this to nitric acid. This acid reacts with calcium compounds to form water soluble calcium nitrate causing severe biodegradation. Reduction of surface pH to 2 and corrosion up to a depth of 20 mm over six months has been reported. **Berndt (2011)** [42] has evaluated coatings, mortars and mix design for protection of concrete against sulfur oxidizing bacteria.

2.5. MICC in Nuclear power plants

Normally nuclear power plants are designed for a life span of 30 – 40 years but with the experience gained in the operation of nuclear reactors, future power plants will be designed for 60 – 100 years to make nuclear power plants more economical. Therefore, integrity of the associated concrete structures especially exposed to aquatic environments has to be maintained, for this duration. Nuclear systems contain safety related concrete structures like foundation, support, biological shielding, containment and cooling water system structures like intake well, intake pipes, pump house well, cooling towers etc.[43] . When safety related concrete structures see the aggressive environment of radioactivity, cooling water systems structures are facing the aggressive seawater conditions. The reinforcement corrosion is a major problem in cooling towers of cooling water system of reactors [44]. According to the **American Concrete Institute (ACI) Report 222** [45]**,** corrosion of Metals in Concrete, under some conditions, a chloride content of as little as 0.15 percent by weight of cement is sufficient to initiate corrosion of embedded steel in concrete while in the presence of oxygen and moisture [46]**.**

2.6. Biodeterioration of cement used to immobilize radioactive waste

Very little information is available on the possible effects of microbes on the concrete or cement paste used to immobilize radioactive and heavy metal wastes. Short-lived isotopes such as strontium and caesium are immobilized in cementious mixtures and buried in soil [47]. **Atkins and Glassner (1992)** [5] got evidence that strontium is absorbed by or precipitated in cement and they proposed the application of Portland cement based materials for immobilization. Studies by **Aviam et al. (2004)** [6]**,** and **Atkinson and Nickerson (1998)** [48] showed the difficulty in immobilizing caesium in cement due to the fact that this element belongs to the alkali monovalent group of metals which are highly soluble.

2.7. Attempts to protect concrete structures from MICC

Nasrazadani and Sudoi (2010) [35] suggested some countermeasures to mitigate damage by microorganisms as follows:

1. Establishment of a regime of inspection or monitoring that immediately detects the appearance of biofilm.
2. Determination of organisms that constitute the biofilm, including its density and location.
3. Elaborate integrated planning against the involved organisms in order to solve the problem.
4. Supervision of the integrated plan and its results.

Depending on the type of organism detected and the degree of damage of the structure, integrated plans can include a combination of the following measures:

- Surface cleaning using chemical agents (i.e. biocides), and biological and chemical means.
- Surface painting using admixtures with biocides.
- Replacement of the concrete cover.

The methods commonly used for the concrete structures protection from biodeterioration include modifications of concrete mix design; coatings that may be sprayed painted or rolled onto the concrete surface and liners. The main aim of concrete mix modification is to increase the alkalinity [12]. Concrete with a water-to-cement ratio w/cm ≤ 0.45, and depth of water penetration < 2.0 cm, and contains special additives like polypropylene and biocides can withstand biological attack. Many workers added additives prepared as bacteriostatic composite systems protecting concrete for a long time [49].

Vincke et al., (2002) [50] studied influence of polymer addition on biogenic sulfuric acid attack of concrete and found that presence of polymers within matrix caused bridging of micro-cracks and pore-size reduction and blocking of pores resulting in reduced concrete permeability. This can reduce ingress of H_2S and penetration of acid producing microbes. **Pavlik and Uncik (1997)** [51] also observed reduction of permeability and diffusivity by addition of silica fume. **Muynck et al. (2009)** [52] tested concretes with hydrous silicate admixture (SAC), epoxy coating (EC), polyurea lining (PUL) and a cementitious coating and also studied concretes with antimicrobial fibres and concretes with antimicrobial zeolites. They found that the best protective performance towards biogenic sulfuric acid corrosion was obtained using epoxy coating. **Seok-kyon Park et al. (2009)** [53] added antimicrobial microcapsules into mortar to eliminate fungal growth on concrete structures. Results showed that the plain mortar concrete specimens without the microcapsules were covered with fungi while there was no fungus observed on the specimens covered with 5% and 15% additions of microcapsules. **Alum et al. (2008**) [54] studies different biocide formulations and found that concrete mixtures containing 10% ZnO was very effective. Cement containing photocatalytic titanium dioxide and exposed to artificial sunlight strongly inhibited fungal colonization and biofouling.

Terry et al. (2000) [55] presented the various types of protective coatings for concrete, as they are the viable method for extending service life while providing improved appearance and additional value to concrete structures. Many workers are recommending simultaneous use of biocides and coatings or biocides addition to coatings [56] to prevent biodeterioration. The growth inhibitory compounds like calcium formate may protect the sewerage systems from the action of sulfur-oxidizing bacteria [57]. Such compounds should not weaken concrete when they are mixed with cement and should not pollute the environments. Different epoxy coatings, different mortars like epoxy-modified cement mortar, latex-modified mortar and calcium aluminate mortar were investigated and **Berndt (2011)** [42] found that the epoxy coatings and calcium aluminate mortar gave the best performance. Partial replacement of cement with 5 to 10% silica fume or 40% blast furnace slag improved concrete resistance to MIC. Acid-proof potassium silicate concrete and an epoxy coating were reported as being successful in resisting MIC due to SOB [58]. **Daczko et al. (1997)** [59] found that silica fume and an organic inhibitor reduced mass loss after 100 days of exposure in sulfuric acid. **Sand et al. (1994)** [60] and **Scrivener et al. (1999)** [61] reported that liners made of calcium aluminate cement provided resistance to SOB in sewers.

Efforts to control corrosion of concrete sewers are directed at two links in the corrosion chain [62]. The first link is protection of concrete with coating [63]. Experience shows that the coatings delaminate due to improper preparation of surface and improper application. Second link targets reduction of harmful gases by continuous and regular dosage of chemicals such as potassium permanganate, chlorine, oxygen injection, directly in raw sewerage. These treatments are costly and are not a lasting solution. According to these workers the ideal method is to permanently affect the bacterial-cell growth or pH of the concrete such that the bacteria no longer grow and convert H_2S to H_2SO_4. Thus an antimicrobial material non-toxic to humans and animals integrated into polypropylene fibre was introduced into the concrete.

Admixtures are chemicals, which are added to concrete at the mixing stage to modify the properties of concrete. They can increase workability, reduce water content, adjust setting time, reduce segregation, increase strength, reduce permeability etc. The use of high range water reducers called superplasticizer has become a common practice in various industries including nuclear industry. Superplasticizers are linear polymers containing sulfonic acid groups attached to the polymer backbone at regular intervals [64]. The commercial formulations belong to one of four families: sulfonated melamine-formaldehyde condensates (SMF), sulfonated naphthalene-formaldehyde condensates (SNF), modified lignosulfonates (MLS) and polycarboxylate derivatives. The sulfonic acid groups are responsible for neutralizing surface charges on the cement particles and enabling dispersion, thus releasing the water tied up in the cement particle agglomerations and thereafter reducing the viscosity of the paste and concrete [65]. The capability of superplasticizer to reduce water requirements 12-25% without affecting the workability leads to production of high-strength concrete and lower permeability.

In our laboratory we initiated a study to compare two types of concrete mixes with no admixture and with admixture and results reported [66]. The ratio of cement: water: and aggregate was 1: 0.45:1.71:2.92 and 1:0.413:1.70: 3.01 respectively. The biofilm formation along with pH reduction was followed on both types of concrete and detailed methodology reported elsewhere. Exposure was done in a tank made of fiber-reinforced plastic (FRP) with seawater. Parameters of interest in biofilm formation were total bacterial density (TVC) using Zobell marine agar, total fungal density with Czapek Dox agar, total density of sulfate reducing bacteria using modified Postgate medium. Biofilm thickness measurements and biochemical parameters evaluation were done. Isolation, screening and characterization of sulfur oxidizing bacteria were done and epifluorescence microscopy was used to observe the biofilm morphology on the concrete surfaces. To compare the species richness on two surfaces, genomic DNA isolation, PCR amplification and sequencing of 16S rRNA genes were done.

The pH estimation of the exposed concrete samples clearly showed a pH reduction both concrete surfaces. However, the reduction was slower on the concrete surfaces that have incorporated SP admixtures. Results also showed that biofilm thickness, total bacterial density, total density of sulfur oxidizers and sulphate reducers were highest on the normal concrete surface compared to concrete surface with admixtures.

Epifluorescence micrographs further confirmed the difference in biofilm intensity on both surfaces (Fig. 3). The comparative studies showed that density of acid producing *Thiobacillus* sp. measured, as the intensity of pH reduction in Starkey broth was also higher on normal concrete surfaces compared to concrete with admixtures (Fig.4). Another significant result in this study was the isolation of high number of sulphate reducing bacteria (SRB), *Desulfovibrio* sp. which complete the sulfur cycle in these biofilms. The density of SRB was also higher in normal concrete (MIX-I) biofilm. Higher density of acid producing *Fusarium* sp., a fungus and higher species richness was seen on normal concrete compared to concrete with admixtures. Thus our study has clearly provided the proof, that an attempt to modify the concrete by addition of superplasticizer admixtures has also provided some resistance to reduction of pH and formation of biofilm in seawater environments.

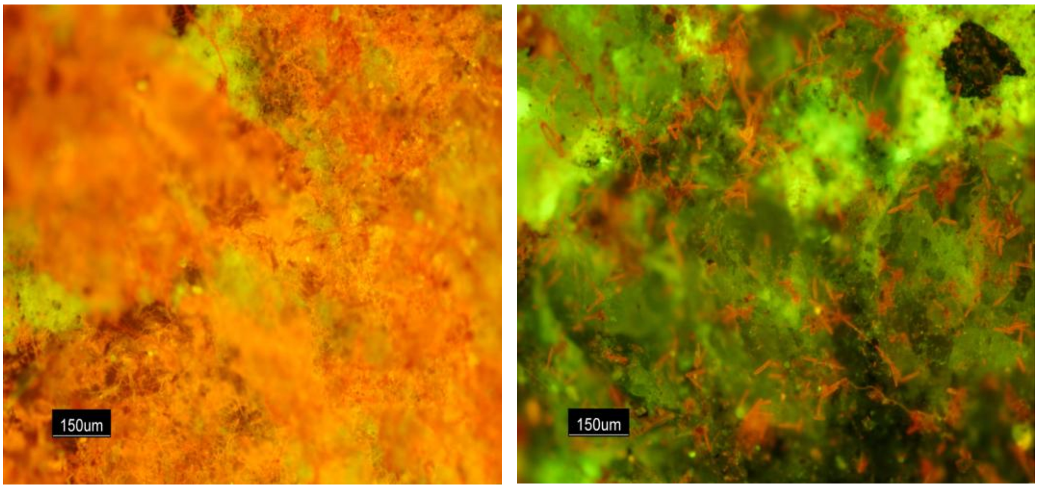

Fig 3: Epifluorescence micrographs of biofilm formation on MIX-I and MIX-II concrete Surfaces showing higher orange fluorescence and thereby higher biofilm density on MIX-I Normal concrete surface compared to MIX-II SP admixture concrete Surface

Fig 4: Growth of SRB indicated in Modified Postgate medium by blackening showing density of SRB higher on normal concrete MIX-I biofilm compared to admixture concrete MIX-2 biofilm

3. Nuclear industry opting for – Fly ash Concrete

In the cooling water systems of nuclear reactors, there are many concrete structures in the form of tanks, pillars and reservoirs that come in contact with seawater. Concrete undergoes several reactions when exposed to aggressive seawater environments. With a high quality or an impermeable concrete skin, the chemical and biological attack by seawater can be limited. And nuclear industry has decided to partially replace the Portland cement with appropriate pozzollans such as fly ash, which could densify the matrix and make the concrete impermeable [67]
The main application of fly ash in concrete is reaction with calcium hydroxide forms compounds that are actually stronger and more durable than concrete made with pure cement. Concrete with Fly ash and cement is also known as *green concrete*. It binds the toxic chemicals that are present in the fly ash in a way that should prevent them from contaminating the natural resources. Using fly ash cement in place of or in addition to Portland cement uses less energy, requires less invasive mining and reduces both resource consumption and CO_2 emissions. It reduced water requirements, increases workability, and reduces bleeding, segregation and heat of hydration. It decreases drying shrinkage, improves water tightness in concrete, reduces Alkali-Silica reactivity in concrete, improves resistance of sulfate and acid attack, long term strength also [68,69].

4. Future Approaches in Better understanding and controlling MICC

4.1. Nanotechnology for high-performance cement composites

The development of nano-science can have a great impact in the field of construction materials too. Portland cement is one of the largest commodities consumed by mankind, but not completely explored. Better understanding and engineering of complex structure of cement based materials at nano-level will definitely result in a new generation of concrete, stronger and more durable, with desired stress-strain behaviour and possibly with the whole range of newly introduced “smart” properties [70]. The particle size and specific surface area scale related to concrete materials was described by **Sobolev et al., 2005** [71]**.** He showed that conventional concrete with a particle size range of 10 µm to 1 cm has a specific surface area of .01 to 100 m^2 /kg. Whereas nanoengineered concrete can have 10 nm size particles like nano silica and surface area of 10, 00,000 m^2/kg. This remarkable surface area can impart improved properties like compactness, self cleaning, antibacterial properties, durability etc. to concrete.

Self compacting concrete (SCC) was an early advancement in concrete technology which showed excellent filling ability, good passing ability and adequate segregation resistance [72]. However, they lacked high strength and good durability which led to the development of high performance concrete (HPC) [73]. Again HPC lacked the good properties of SCC and hence it is ideal to develop concrete that combines the performance criteria of SCC and HPC which can be the new generation concrete referred to as SCHPC. The final performance of concrete depends on the strength and water permeability. Hence mechanical and physical properties enhancement should go hand in hand to develop high performance cement composites. Addition of nanoparticles with enhanced physical and mechanical properties to SCC can make SCHPC. Many workers added nano SiO_2 [74], nano Al_2O_3 [75], nano Fe_2O_3 [76] and zinc-iron oxide nanoparticles [77] for betterment of mechanical properties and permeability. The addition of dispersion or slurry of nanosilica improves segregation resistance for self compacting concrete [78].

Li (2004) [79] found that addition of nano SiO_2 could significantly increase the compressive strength of concrete which contain large volume of fly ash, especially at the early stage and improve pore size distribution by filling the pores between large fly ash and cement particles at nano scale. **Mann (2006)** [80] reports that addition of small amounts of carbon nanotubes (1%) by weight increase both compressive and flexural strength. One major concern with the structures is the cracking problems. **Kuennen (2004)** [81] is working on healing polymers that involves microencapsulated healing agent and a catalytic chemical trigger. As the crack breaks the microcapsules, the healing agent is released and this comes in contact with the catalyst. The self-healing polymer will be able to fix the crack.

Nazari and Riahi (2010) [82] studied the effect of TiO_2 nanoparticles on water permeability and thermal and mechanical properties of high strength self-compacting concrete. The results indicated that the strength and the resistance to water permeability of the specimens are improved by adding TiO_2 nanoparticles in the cement paste up to 4.0 wt%. These nano TiO_2 increased the crystalline $Ca(OH)_2$ amount especially at the early stage of hydration, and this could accelerate C-S-H gel formation and hence increase the strength of concrete. In addition these nano TiO_2 also act as nanofillers and decreased harmful pores and provide antibacterial activity to the concrete.

The efficacy of the addition of nano-$CaCO_3$ in accelerating the hydration of ordinary Portland cement (OPC) delayed by the presence of high volumes of supplementary cementitious materials including fly ash and slag was investigated [83]. They found that addition of nano $CaCO_3$ significantly accelerated early hydration of OPC and it was directly proportional to the amount added. Microhardness and modulus of elasticity was improved remarkably by the nano addition. According to these workers the seeding effect of nano $CaCO_3$ particles and nucleation of C-S-H caused the enhanced strength development. **Xu et al. (2011)** [84] studied effect of nano $CaCO_3$ on the compressive strength and microstructure of high strength concrete in different curing temperatures and reported that 1% and 2% dosage of nano-CaCO3 could improve the strength of the concrete by 13% and 18% in standard curing temperature and by 17% and 14% in low curing temperature at the age of 3days.

Raki et al. (2010) [85] has described the potential of improving the concrete properties by modifying the structure of cement hydrates, addition of nanoparticles and nanotubes and controlling the delivery of admixtures. They have presented a nanotechnology based approach for controlled release of admixtures using layered double hydroxides (LDH). The controlled release formulation provided a longer time for the superplasticizer to keep cement workability at a reasonable level after mixing and alleviated the difficulties associated with slump loss.

Despite all this work, detailed evaluations of nanomaterials is required to introduce their characteristics and effects on cementitious materials. Origin of most process in cementitious materials is at nanoscale. Concrete has a complex nanaoscale structure which plays a critical role in determining various properties. For example, capillary forces in partially saturated pores less than 100 nm control shrinkage and cracking. Absorption of superplasticizer molecules on cement grains controls rheology. The main hydrate phase C-S-H controls strength, durability of the concrete structures. Thus further research in nanotechnology promises breakthroughs in several areas like avoiding early age cracking, increasing strength, minimizing concrete and reinforcement deterioration due to chemical and biological attack.

5. Conclusions

This overview paper has tried to compile the status of knowledge in the field of biodeterioration of concrete, identify areas where more information is needed, and describe nanotechnologies that can be used to obtain the research goals.

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