Antimicrobial concrete for smart and durable infrastructures: a review

Liangsheng Qiu[1], Sufen Dong[2, *], Ashraf Ashour[3], Baoguo Han[1, *]

[1]*School of Civil Engineering, Dalian University of Technology, Dalian, 116024 China*
[2]*School of Material Science and Engineering, Dalian University of Technology, Dalian, 116024 China*
[3]*Faculty of Engineering & Informatics, University of Bradford, Bradford, BD7 1DP, UK*
* Corresponding author: hanbaoguo@dlut.edu.cn, dongsufen@dlut.edu.cn

Abstract

Concrete structures in sewer systems, marine engineering, underground engineering and other humid environments are easily subjected to microbial attachment, colonization and, eventually, deterioration. With careful selection and treatment, some additives including inorganic and organic antimicrobial agents were found to be able to endow concrete with excellent antimicrobial performance. This paper reviews various types of antimicrobial concrete fabricated with different types of antimicrobial agents. The classification and methods of applying antimicrobial agents into concrete are briefly introduced. The antimicrobial and mechanical properties as well as mass/weight loss of concrete incorporating antimicrobial agents are summarized. Applications reported in this field are presented and future research opportunities and challenges of antimicrobial concrete are also discussed in this review.

Keywords: Concrete; Antimicrobial; Properties; Mechanisms; Applications

Content

1. Introduction

Concrete is the most widely used construction material for various infrastructures worldwide. However, concrete structures in certain aggressive environments, such as sewer systems, marine engineering, buildings exposed to high humidity and the like, are easily suffered from microbial attachment, colonization, eventually, deterioration [1-4]. For example, the most typical problem faced by reinforced concrete structures in sewer systems is microbial induced corrosion, which is still commonly referred to as a sulfide (H_2S) gas problem. The process initiated when sulfate-reducing bacteria (SRB) convert sulfate into hydrogen sulfide gas under anaerobic conditions, that is converted into corrosive sulfuric acid by sulfur-oxidizing bacteria (SOB) of the genus Thiobacillus [1,5-11]. Some fungi also participate in this activity [12,13]. Concrete structures in the tidal and splash zones of marine concrete engineering are dominantly damaged by Pseudoalteromonas, along with Vibrio, Pseudomonas and Arthrobacters, etc. [14, 15]. Bio-deterioration of concrete in irrigation and hydroelectric canals [16], spots or patches covered on concrete walls [17], and biological decay of mortars on building facades [18] commonly result from the growth of algae and cyanobacteria. Algal growth is also quite common on concrete walls of water storage and conveyance structures [19]. Salmonella, an important foodborne pathogen, are easily attached and colonized on surfaces of concrete used in food industry due to their adherence forming biofilms [20]. The propagation and proliferation of microorganisms including bacteria (e.g., pathogens), fungi, and algae alone or together, on and/or in concrete structures, will affect concrete's aesthetic appearance, destroy the internal structure of concrete, degrade mechanical properties and durability of concrete, increasing the cost by rehabilitation and even replacement [2, 16, 21-23]. Therefore, developing antimicrobial concrete for smart and durable infrastructures has become extremely significant and imperative.

Researchers have been attempting to develop antimicrobial concrete (concrete is a collective term referring to concrete, cement mortar and cement paste as well as cementitious/cement-based materials/composites in this paper) by adding some additives having antimicrobial properties for sterilization against a specific microorganism or multiple microorganisms, meanwhile without significantly impairing concrete essential properties such as compressive strength. The last two decades have witnessed an ever-increasing growth in studies on the utilization of functionalized zeolites supporting bactericidal metal ions, such as silver, copper and zinc ions [24-27]. Haile et al. [28-30] reported that concrete containing silver bearing zeolite exhibited antimicrobial characteristics against Acidithiobacillus thiooxidans (A.thiooxidans), as reflected by inhibition of formation of A.thiooxidans biofilm. Further, Xu [31] and Li [32] reported that concrete added with silver-loading zeolite and polypropylene fiber exhibited obvious bactericidal effect towards Escherichia coli (E. coli). Moreover, it is reported that antimicrobial concrete containing Zeomighty (zeolites with silver and copper ions) was introduced on the Japanese market [33]. Quaternary ammonium compounds (Quats) have been used as antimicrobial agents for a long time, and only recently they have been reported to be effective as algaecides [11, 16, 19, 34]. Intentionally, considering the severe consequences caused by microbial induced corrosion of concrete, considerable attention has been paid to find effective antimicrobial agents to admix into concrete in order to fight against Thiobacill [3, 23, 35, 36]. For instance, Shook and Bell [37] reported that ConShield, added into concrete during the mixing stage, showed high sterilizing rate and stable bactericidal effect against Thiobacillus bacteria. Yamanaka et al. [38] found that calcium formate was able to completely inhibit the growth of both sulfur-oxidizing and acidophilic iron-oxidizing bacteria at concentrations above 50 mM. Some investigators tried to develop antimicrobial concrete by incorporation of nickel, and tungsten specially targeting at SOB which play a dominant role in biogenic corrosion of sewer systems [39-43]. Sun et al. [44] verified the strong bactericidal effect of free nitrous acid (FNA) on microorganisms due to cells in corrosion biofilms of concrete surfaces were killed. In addition, the combination of water repellents (decrease bio-receptivity) plus biocides (decrease biological activity) has been reported to be effectively inhibiting microbial growth in mortars, white concretes and autoclaved aerated concretes [45, 46]. Vaquero et al. [16] proposed a novel cement-based material with biocidal activity that can be used as an overlay of mortar in existing structures, such as canals and pipes.

In recent years, with the rapid development of nanotechnology, some researchers have tried to introduce some nano-particles into concrete to inhibit microbial colonization. For example, the research undertaken by Singh et al. [47] indicated that cement-ZnO composite possesses effective antibacterial and antifungal activities under dark and solar light due to the addition of ZnO nano powder. Wang et al. [48]

demonstrated that high performance concrete (HPC) incorporated with nano ZnO has antibacterial ability against E. coli and Staphylococcus aureus (S. aureus). Concrete fabricated with titanium dioxide nanoparticles has great potential in sterilization under the light [49]. Ganji et al. [50] found that cement with nano-TiO_2 inhibit the growth of E. coli under UV irradiation. Moreover, Fonseca et al. [18] proposed that anatase can be an alternative application for preventing bio-deterioration of mortars.

This paper is intended to summarize antimicrobial concrete fabricated with different types of antimicrobial agents, intuitively shown in Fig. 1. First, the classification of antimicrobial agents and their application methods into concrete are briefly introduced. Then, the antimicrobial and mechanical properties as well as mass/weight loss of concrete incorporated with antimicrobial agents are reviewed, with emphasis on antimicrobial properties. Subsequently, antimicrobial mechanisms of some inorganic and organic antimicrobial agents were explicated. Finally, applications of antimicrobial concrete in sewer systems, marine engineering and buildings against microbial threat are also presented.

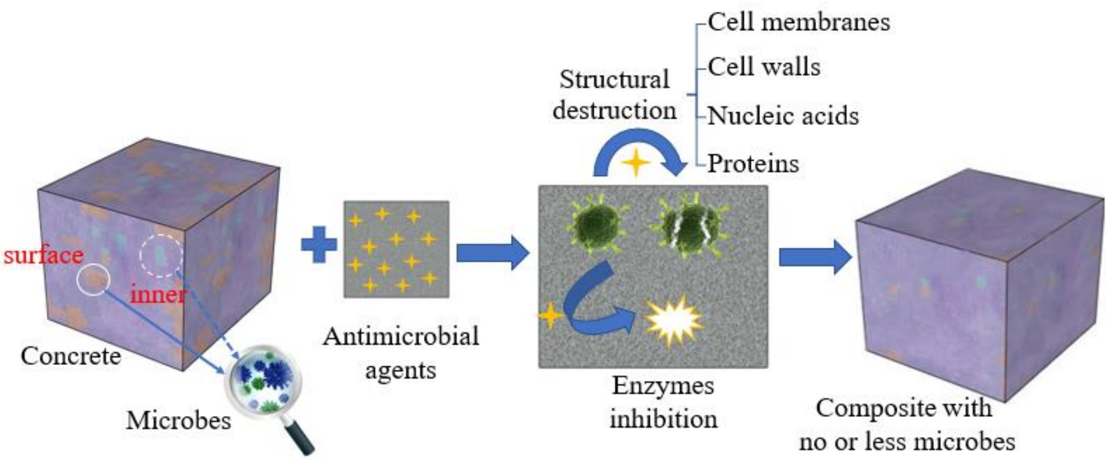


Fig. 1 Schematic diagram of antimicrobial concrete.

2. Classification of antimicrobial agents used for fabricating antimicrobial concrete

The antimicrobial property of antimicrobial concrete was attributed to the addition of antimicrobial agent, which is a collective name herein for the mentioned antimicrobial additives facilitating concrete to inhibit and/or kill various microbes including bacteria (e.g., pathogens), fungi, and algae. Antimicrobial compounds including biocides, microbicides, sanitizers, antiseptics and disinfectants characterized by their ability of killing microorganisms and/or inhibiting microbial reproduction, are easily accessible [23,34]. The antimicrobial agents reported to have been added to concrete ingredients can be classified into inorganic and organic antimicrobial agents with respect to their chemical composition as detailed below.

2.1 Inorganic antimicrobial agents

Inorganic antimicrobial agents that have been reported to be applied in concrete include heavy metals (silver, nickel, tungsten), metal compounds (silver molybdate, copper oxide, zinc oxide, sodium tungstate, sodium bromide), NORGANIX (a silicate concrete sealer), free nitrous acid (FNA), and nano inorganic antimicrobial materials. The antibacterial activity of metal or metal ions is in the order of: Ag>Hg>Cu>Cd>Cr>Ni>Pb>Co>Zn>Fe [22,32,51,52]. Although silver ion antibacterial agent series are effective but considering their high cost, few other alternatives with high bactericidal effect were explored in the literature. For example, Zhang [22] found that cerium nitrate exhibited an excellent antibacterial effect in porous concrete, even with a low content of 1.25%. Furthermore, the use of nanomaterials to control microbial colonization of concrete has considerably increased in recent years [53]. Nanoparticles (NPs) of Cu_2O, $CaCO_3$, TiO_2, ZnO, CuO, Al_2O_3, Fe_3O_4, etc., were reported to exhibit inhibitory effects against a wide range of microorganisms in this field [3, 4, 26, 47,48, 54, 55].

2.2 Organic antimicrobial agents

Quats, phthalocyanine compound (including metal organic antimicrobial agent copper phthalocyanine), calcium formate, alkyl nitro-bromide (A II B), isothiazoline/cabamate, ConShield (a highly charged cationic polymer), and ConBlock MIC (whose active ingredient is 3-Trimethoxy silyl propyl dimethyl octadecyl ammonium chloride) are various organic antimicrobial agents used in concrete. Additionally, Freed et al.[56] proposed that fibers incorporated with at least one antimicrobial agent, such as Microban B (a phenol-based antimicrobial agent), were able to inhibit microorganisms. Quats are the most representative organic antimicrobials, e.g., silane quaternary ammonium chloride(SQA)[57], and cetyl-methyl-ammonium bromide [19], which have been widely studied and applied by researchers [23, 51, 58]. Isothiazoline/cabamate is a type of organic antifungal agents, often used to target at Aspergillus niger which is easily found in the interiors and exteriors of buildings in damp environment [59]. Uchida et al. [11] stated that water pollution as a result of metal eluted into sewage can be addressed by adding a phthalocyanine compound (a metal phthalocyanine, a metal-free phthalocyanine, and derivatives thereof) into concrete, which will not pollute water and a small amount of inhibitor can prevent deterioration of concrete or mortar due to SOB for a long time.

Generally, inorganic antimicrobial agents have long service life and high temperature resistance, but have side effects like toxicity. Organic antimicrobial agents possess obvious bactericidal effect in a short term and broad spectrum of killing activity but their temperature resistance is poor [22,31,32,60]. Moreover, most of organic biocides are ultimately ineffective at removing microbes and may eventually lead to a new wave of microbes on the affected surfaces after microbes develop a resistance [34]. The following sections will describe these antimicrobial agents and their methods of applications in detail.

3. Methods of applying antimicrobial agents into concrete

Some antimicrobial agents use inorganic or organic cementitious materials as carriers to form protective coatings, with biocidal property on concrete surfaces [23,35]. Another method to apply antimicrobial agents into concrete is directly incorporating antimicrobials into concrete mix as functional components after pre-dispersion [23,35]. For example, calcium formate was added in the mixture[38], ConShield was incorporated into the mix and the protection was throughout the entire thickness of concrete matrix [37]. The antimicrobial watertight admixture made of fluosilicate salts and antimicrobial compounds (Ni and W) [61] is in liquid state to be homogeneously dispersed in concrete. The phthalocyanine compound [11] can be dispersed uniformly in concrete or mortar by a blending agent selected from a group consisting of an air entraining agent, a water reducing agent, and a viscosity increasing agent. Liquid bactericides like dimethyl benzyl ammonium chloride can be made into powder adsorbed by carrier such as zeolite [23, 62]. In addition, heavy metal antibacterial agents are usually fixed on zeolites by means of adsorption or ion exchange [27,51,63]. Known as crystalline pozzolanic aluminosilicate minerals with uniform molecular sized pores, zeolites can be functionalized to exhibit antimicrobial property if calcium and sodium ions in their framework are exchanged by silver, copper or zinc ions, explaining that zeolites are the most common carriers of inorganic metal ions [3, 26, 27, 29, 51, 63, 64].

Agglomeration due to high activity of antimicrobial nanoparticles in cement matrix is a common concern, significantly decreasing their chemical and physical activities and, hence, affecting their efficiency in cement matrix performance and antimicrobial activity [49, 60]. A dispersion medium (most likely mixing water) and incorporation of organic admixtures and different surfactant types, e.g., plasticizers and superplasticizers, facilitate to address the issue of homogeneous dispersion in the cement matrix, as presented in Fig. 2 [49, 54]. It is also reported that the application of superplasticizer in photocatalytic cement can enhance nano-TiO_2 dispersion in samples by preventing agglomeration of titanium dioxide in cement pastes, which is also conducive to improve the contact between titanium dioxide and bacteria, contributing to better bacterial inactivation [50]. However, in the case of antimicrobial agents being functional components in concrete, the selection of biocide types and contents has not been systematically investigated [35, 65].

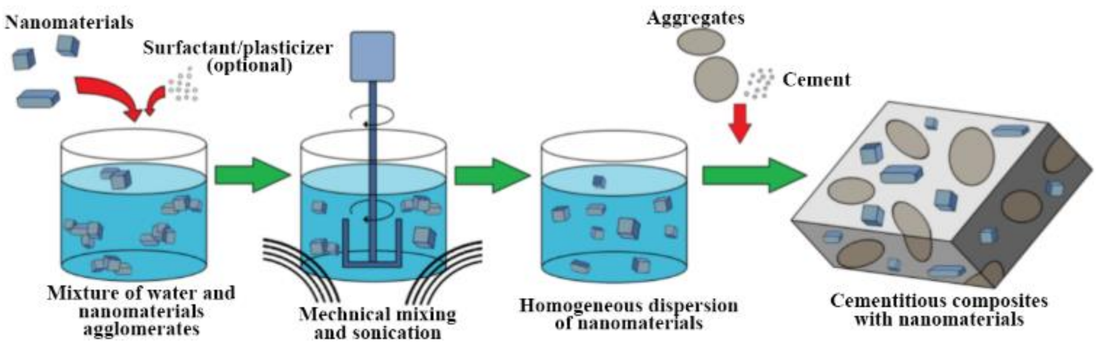


Fig. 2 Schematic process of nanomaterials dispersing method commonly used in cement-based composites preparation [54].

4. Properties of antimicrobial concrete

4.1 Antimicrobial property

4.1.1 Antimicrobial concrete with inorganic antimicrobial agents

The antimicrobial property is the most important assessment factor for antimicrobial concrete, that varies with the addition of different types of antimicrobial agents, as summarized in Table 1. Antimicrobial concrete, with the addition of diverse antimicrobial agents against microorganisms involving in microbial induced corrosion, especially in sewer systems, have been extensively studied in the literature. Nickel and tungsten have been known to protect concrete from microbial corrosion owing to their antimicrobial effect towards causative bacteria, i.e., Thiobacillus thiooxidans (T.

thiooxidans). Negishi et al. [41] found that the cell growth of A. thiooxidans, including strain NB 1-3 (isolated from corroded concrete in Fukuyama, Japan) was strongly inhibited by 20 μM sodium tungstate, and completely inhibited by 50 μM sodium tungstate. Similarly, Sugio et al. [42] reported that cell growth of an iron-oxidizing bacterium, Acidithiobacillus ferroxidans (A. ferroxidans), was strongly inhibited by 0.05 mM and completely inhibited by 0.2 mM of sodium tungstate. In the study of Maeda et al. [40], concrete containing 0.1% metal nickel and concrete with 5 mM nickel sulfate were found to completely inhibit the cell growth of strain NB 1-3 of T. thiooxidans isolated from corroded concrete. Moreover, Kim et al. [61] conducted an investigation to evaluate the antibiosis of antimicrobial ingredients (Ni and W) of antimicrobial watertight admixture mixed in mortar and concrete on Thiobacillus novellus (T. novellus). Broth Microdilution MIC test indicated that T. novellus could not survive in the area where the admixture is dropped. As reflected in Table 1, the total colony test numerically shows that T. novellus in culture solution with mortar added with the admixture were disappeared after 24 h. The biochemical corrosion simulation test also indicated that the number of T. novellus was much lower in the case of mortar mixed with the admixture than plain mortar specimens. The results suggested that the addition of antimicrobial watertight admixture in cement mortar and concrete suppressed the growth of T. novellus. Furthermore, Southerland et al. [66] found that tungsten used alone is able to inhibit growth of T. novellus, whereas molybdenum, ammonium molybdate or a mixture of ammonium molybdate and tungstate activates growth of the same bacteria. Likewise, it is reported that molybdenum activates growth of T. novellus but inhibits growth of T. thiooxidans, indicating SOB of the same genus Thiobacillus have different growth inhibitory mechanism. It is noteworthy that the antimicrobial property of antimicrobial agent Ni and W is not only largely dependent on their contents, but greatly affected by pH. It is generally recognized that nickel compounds are suitable for neutral environment, while tungsten compounds are more effective in acidic environment [23, 43]. Maeda et al. [40] observed that the amount of nickel contained in the strain NB 1-3 cells treated without nickel, treated with 10 mM nickel sulfate at pH 3.0 and treated with 10 mM nickel sulfate at pH 7.0 was 1.7, 35 and 160 nmol nickel per mg protein, respectively. The results indicated that nickel is able to bind to strain NB 1-3 cells, and much more nickel binds to the cells at neutral pH than at acidic pH demonstrated that nickel ions have a better inhibitory effect towards the microbe in neutral environment than in acid environment [40]. The findings of Negishi et al. [41] and Sugio et al. [42], as detailed in Table 1, demonstrated that the antimicrobial property of tungsten is more effective in acidic environment than in neutral environment.

Furthermore, Kong et al. [62, 65] conducted an investigation to evaluate the impact of adding five bactericides in concrete towards the selected bacteria (as listed in Table 1), and to study their applicability for controlling and preventing microbial corrosion of concrete. They reported that concrete with sodium bromide and zinc oxide exhibited excellent antimicrobial property towards the tested bacteria, especially Bacteroidetes, as the number of microbial populations decreased substantially. However, the antimicrobial effect of concrete with a dispersion of sodium tungstate on microbes is worst, as reflected by the lowest bactericidal rate (21.95%), it even promotes the growth and reproduction of Proteobacteria. They also observed the dead and live microorganisms within biofilm with confocal scanning laser microscopy (CLSM), as seen in Fig. 3. The number of live cells within the biofilm all decreased to a certain degree, indicating all the tested bactericides have a certain sterilizing effect. Similarly, Bao [67] obtained that the surface roughness of the control mortars and mortars with sodium tungstate and sodium bromide was 46.65, 14.3 and 9.02 μm after a 3-month immersion in intensified sewage, respectively. Therefore, they concluded that the addition of sodium tungstate and sodium bromide could effectively inhibit the growth and reproduction of microorganisms attached to the surface of cement mortar. In addition, Sun et al. [44] studied the bactericidal effect of FNA on microbes in sewer biofilms of two concrete coupons. They observed that, as for the intact corrosion biofilm, H_2S uptake rates (SUR) were reduced markedly 15 days after FNA spray and viable bacterial cells severely decreased by over 80% within 39 h (detailed in Table 1), suggesting that biofilm cells were killed by the treatment. As for a suspended solution of corrosion biofilms scraped from the concrete coupon, ATP level and ratio of viable bacterial cells were also severely decreased by the treatment, as clearly seen in Fig. 4, demonstrating that FNA strongly deactivates bacteria of acidic corrosion biofilm [44].

Table 1. Summary of different inorganic antimicrobials on antimicrobial property

Antimicrobial	Microorganism	Matrix	Findings
Sodium bromide, zinc oxide, sodium tungstate [65]	Bacteroidetes, Proteobacteria, Firmicutes and Actinomycetes	Concrete	High sterilizing rate of NaBr, ZnO towards Bacteroidetes was 86.80%, 79.19%, respectively Na_2WO_4 showed the lowest bactericidal rate as 21.95% towards all bacteria
Silver-loaded zeolite [30]	A.thiooxidans	Concrete	Growth of planktonic and biofilm populations of A.thiooxidans was inhibited
Zinc and silver loading zeolite [29]	A. thiooxidans	Concrete	Functionalized zeolite coated concrete specimens with epoxy to zeolite weight ratios of 2:2 and 1:3 had negligible biomass growth and acid production rates
Silver/copper zeolite, silver/zinc zeolite [28]	A.thiooxidans	Mortar	Co-cations such as Zn^{2+} and Cu^{2+} increases antimicrobial activity of silver bearing zeolite

Nano-copper oxide [26]	A.thiooxidans	Concrete	Higher leaching rate of copper from loosely adhered nano-copper oxide film significantly inhibited the activity of A.thiooxidans
Silver copper zeolites [25]	E. coli, Listeria monocytogenes, Salmonella enterica or S. aureus	Mortar	Centration of silver copper zeolites to obtain a bactericidal effect on mortar surfaces is required more than 3%
Zeomighty [33]	Thiobacilli	N.A.	A concentration of metal zeolites of 1% to cement weight is optimum for suppressing the growth of Thiobacilli
Sodium tungstate [41]	A. thiooxidans	N.A.	Approximately 10 times more tungstate bound to the cells of A. thiooxidans at pH 3.0 than at pH 7.0
Sodium tungstate [42]	A. ferroxidans	N.A.	Approximately 2 times more tungsten bound the cells of A. ferroxidans at pH 3.0 than at pH 6.0
Metal (Ni,W) compounds, $ZnSiF_6$ [61]	T.novellus	Mortar, concrete	Mortar with antimicrobial watertight admixture had higher pH(6.8) and lower concentration of sulfuric acid(3.78×10^{-8} mol/L) compared to that (6.6 and 2.56×10^{-7} mol/L) of plain mortar
Zinc oxide, sodium bromide, copper slag, ammonium chloride, cetyl-methyl-ammonium bromide [19]	Algae	Mortar	Adding 20 wt.% zinc oxide and 20 wt.% sodium bromide exhibited the most effective algal inhibition under laboratory condition The addition of 20 wt.% sodium bromide and 10 wt.% cetyl-methyl-ammonium bromide (an organic antimicrobial agent) showed highest inhibitory effects at under field condition
FNA [44]	N.A.	Concrete	H_2S uptake rate decreased by 84-92% 1-2 months and viable bacterial cells reduced from 84.6±8.3% to 10.7±4.3% within 39 h after FNA spray.

Silver molybdate [52]	E. coli and S. aureus	Concrete	The residual colony count of E. coli and S. aureus is 0 cfu/mL by addition of 0.004% silver molybdate
Cerium nitrate [22]	E. coli	Concrete	Bacterial concentration reduced drastically from 7.50 to 0.01,0,0.02 million per ml after 48 h when the content was 1.25,5.00,10.00%, respectively.
Nano sized TiO_2, $CaCO_3$ [4]	Pseudomonas, Fusarium, algae, blue-green algae and manganese oxidizing bacteria	Mortar	Nano-TiO_2 modified fly ash mortar and nano-sized TiO_2, $CaCO_3$ modified fly ash mortar exhibited enhanced antibacterial activities compared to nano-$CaCO_3$ modified fly ash mortar
Anatase [18]	Cyanobacteria and chlorophyta species	Mortar	Two types of mortars with different kinds of sand showed the lowest photosynthetic growth ratio (0% and 0.03%, respectively)
SiO_2/TiO_2 nano-composite [68]	E. coli	Cement mortar	Bacteria inactivation after UV light irradiation and without illumination after 120 min was 67% and 42%, respectively.

Note: A. thiooxidans: Acidithiobacillus thiooxidans; T. thiooxidans:Thiobacillus thiooxidans; T. novellus: Thiobacillus novellus; A. ferroxidans: Acidithiobacillus ferroxidans; E. coli: Escherichia coli; S. aureus: Staphylococcus aureus; N.A.: not available

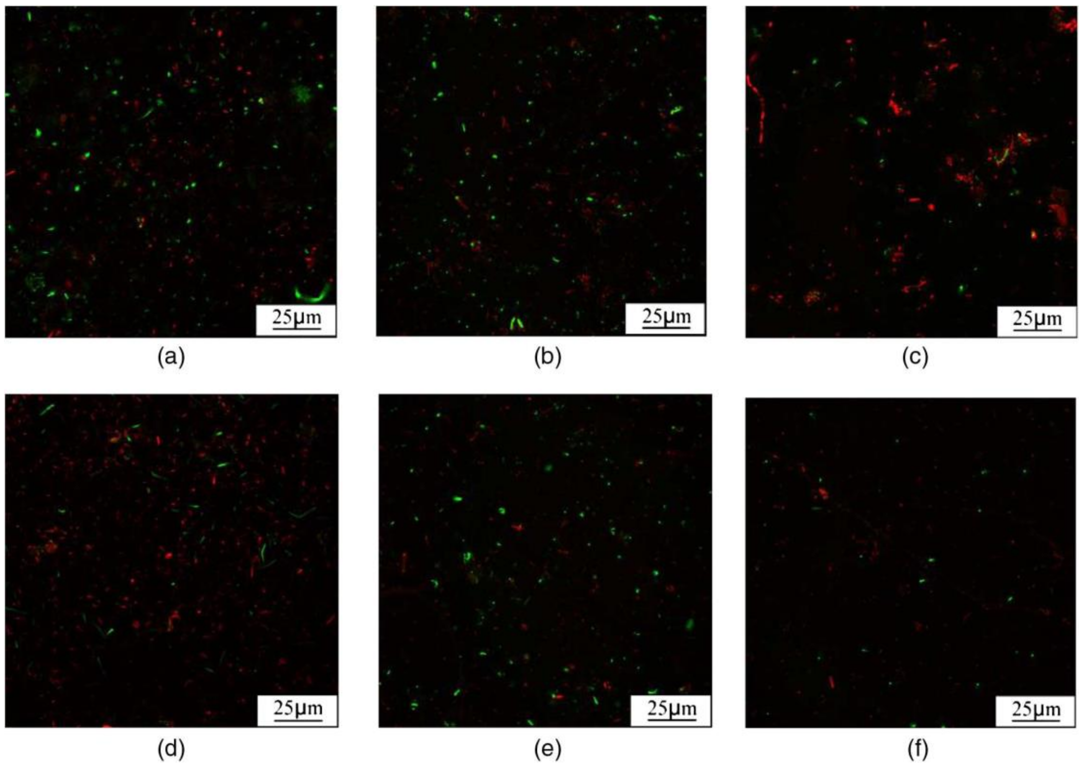


Fig. 3 CLSM images of the distribution of dead/live cells within biofilm attached to concretes: (a) plain concrete without bactericide; (b) concrete with dodecyl dimethyl benzyl ammonium chloride; (c) concrete with sodium bromide; (d) concrete with zinc oxide; (e) concrete with sodium tungstate; and (f) concrete with copper phthalocyanine [62]. Note: living and dead cells are displayed in green and red, respectively, under blue light.

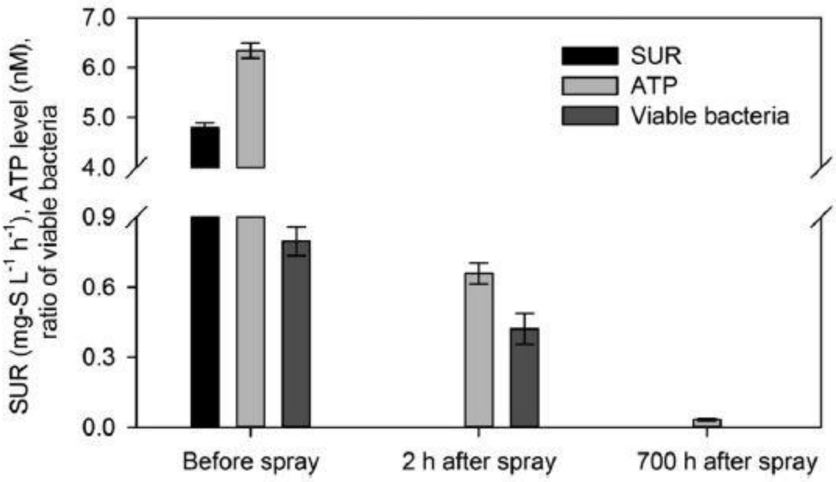


Fig. 4 Levels of SUR, ATP and the ratio of viable bacteria measured on reactor solutions containing the suspended corrosion biofilm scraped from a concrete coupon after 40 months of exposure prior to and after FNA treatment. The ratio of viable bacteria was not determined after 700 h of FNA treatment as cells could not be extracted from the reactor solution [44]. Note: SUR means H_2S uptake rate.

Zeolite containing metal ions has been investigated a lot to be used in concrete due to its excellent antimicrobial property. For example, Haile et al. [28] evaluated the antimicrobial characteristics of mortar specimens coated with silver bearing zeolite with A. thiooxidans. They observed that biomass concentration of A.thiooxidans dry cell weight (DCW) of control specimens (236 mg TSS/L and 181 mg TSS/L) was as much as 2-fold higher compared to the mortars coated with silver-loaded zeolite (125 mg TSS/L and 80 mg TSS/L). The reduced microbial numbers evidenced that the mortar specimens coated silver bearing zeolite exerted antimicrobial characteristic on A.thiooxidans and inhibited bacterial growth. They also found that bacteria were not affected in the nutrient solution indicated that the antimicrobial characteristics of zeolitic coatings were only apparent on solid surface particles [28]. Moreover, Haile et al. [30] discovered that no biomass growth was observed upon exposure of the bacterium to silver-loaded zeolite coated concrete specimens, and there was no oxygen uptake measured, meaning no viability of A. thiooxidans cells for the silver-loaded zeolite coated concrete specimens. The research results confirmed that zeolite containing 5 wt.% Ag is inhibitory to planktonic and biofilm of A. thiooxidans [30]. Similarly, De Muynck et al. [69] observed that mortar specimens with silver-copper zeolites (zeolites contain 3.5% silver and 6.5% copper) obtained a 12-fold decrease of ATP content after 24 h, while inhibition of antimicrobial fibers on bactericidal activity was limited, indicating biocidal effect towards SOB was limited in the case of antimicrobial fibers and that of antimicrobial zeolites was much better. Moreover, De Muynck et al. [25] investigated the antimicrobial effectiveness of silver copper zeolites against E. coli, Listeria monocytogenes, Salmonella enterica or S. aureus in a quantitative way. A clear decrease in the total ATP content was observed for mortar specimens containing silver copper zeolites, indicating the occurrence of antimicrobial activity by the presence of silver and copper ions. Furthermore, they concluded that the concentration of silver copper zeolites is required to be more than 3% so as to obtain a bactericidal effect on mortar surfaces [25]. In the experiment of Haile et al. [70], cellular ATP in concrete contained 2.6 wt.% silver-loaded chabasite declined to zero with a corresponding DCW value of 35 mg, indicating there was no growth after bacteria were exposed to 2.6 wt.% silver-loaded chabasite, whereas the biomass was 51 mg DCW and cellular ATP was 0.21 mg for concrete coated 18 wt.% silver-loaded chabasite. The results indicated that antibacterial characteristics of concrete specimens coated with 2.6 wt.% is superior to the specimens with 18 wt.% silver-loaded chabasite. The results of the experiment conducted by Xu and Meng [64] indicated that the content of E. coli in concrete incorporating silver-bearing zeolite and polypropylene fiber was reduced compared to the control samples, demonstrating that silver-bearing zeolite and polypropylene fiber play a bactericidal role and reduce the breeding of E. coli. Likewise, Li [32] discovered that concrete specimens added with 0.5% silver-loading zeolite and polypropylene fiber had the most pronounced bactericidal effect towards E. coli, as reflected by the greatest OD value (the greater the OD value, the lower the bacterial concentration of the concrete samples) according to antibacterial test results. While antimicrobial effect of concrete specimens incorporated with fly ash and mineral powder was not evident.

Researchers have paid much attention to the effect of antimicrobial nanoparticles on antimicrobial property of concrete. Singh et al. [47] admixed ZnO nano powder into cement composite and evaluated the antimicrobial effect of the formed cement-ZnO composites against two bacterial strains E. coli, Bacillus subtilis and fungal strain Aspergillus niger. As shown in Fig. 5, the antibacterial and antifungal effects of cement-ZnO composite increased as the ZnO concentration increased in the range of 0,5, 10, 15 wt.%. Moreover, it was also noted that both antibacterial and antifungal activities of cement-ZnO composite was enhanced under sunlight compared to dark condition. In addition, Wang et al. [48] conducted a research to study the antimicrobial effect of high-performance concrete (HPC) added with nano ZnO against E. coli and S. aureus. The results showed that the antibacterial rate of the two groups of antibacterial concrete against E. coli reached 100%, however the antibacterial rate against S. aureus was 54.61% and 99.12%, respectively. Through SEM observations, it is found that nano ZnO and its resulting compounds precipitation adhered to surface of cement hydrate, thus inhibited the growth of bacteria, accounting for the significant antibacterial effect of HPC [48]. Sikora et al. [54] conducted a series of tests to evaluate the antimicrobial effect of four metal oxide nanoparticles (Al_2O_3, CuO, Fe_3O_4, ZnO) used in cement-based composites. They discovered that all the studied nanoparticles inhibited microbial growth, and the growth kinetics showed that the highest inhibitory effect on E. coli ATCC® 8739™ and E. coli MG 1655 was Fe_3O_4 nanoparticles, ZnO nanoparticles, respectively. The biofilm formation assay indicated that the tested nanoparticles were able to reduce the formation of bacterial biofilms, E. coli ATCC® 8739™ biofilms were inhibited by all nano-oxides, ZnO nanoparticles significantly affected the formation of P. aeruginosa and S. aureus biofilms. However, the viability of P. aeruginosa cells in sample with Al_2O_3 was significantly higher compared to the control sample. Similarly, Dyshlyuk et al. [71] evaluated antibacterial and fungicidal properties of ZnO, TiO_2 and SiO_2 nanoparticle solution by interaction with eight types of microorganisms commonly causing bio-damage to buildings and concrete structures. They found that ZnO nanoparticles of 2-7 nm in size with a suspension concentration of 0.01-0.25% displayed the most noticeable antimicrobial properties against the tested strains, decreasing microorganisms by 2-3 orders of magnitude. They also revealed that ZnO nanoparticles interacted specifically to a microorganism type, leading to a decrease in the number of Bacillus subtilis B 1448 bacterium by 2 orders of magnitude, and that of fungi of Penicillium ochrochloron F 920 by 3 orders of magnitude. However, TiO_2 and SiO_2 nanoparticles exhibited a low antimicrobial activity. Nano-TiO_2, with its excellent photocatalytic effect, has aroused much interest of many researchers in the aspect of microorganism inactivation. For instance, Ganji et al. [50] investigated the antimicrobial performance of cement samples containing 1,5 and 10 wt.% nano-TiO_2 against E. coli under UV irradiation. They found that bacterial inactivity enhanced as the amount of TiO_2 nanoparticles in cement samples increased, however, the inactivation effect was not obvious even the amount of TiO_2 nanoparticles further increase to 10 wt.%. Therefore, 5 wt.% TiO_2 is proposed to be the most proper content in cement samples for inactivation of E. coli taking into account both the photocatalytic inactivation and cost. Linkous et al. [72] employed nano-TiO_2 in concrete to inhibit the attachment and growth of oedogonium. They discovered that concrete containing 10 wt.% TiO_2 nanoparticles obtained a 66% reduction in the growth of oedogonium.

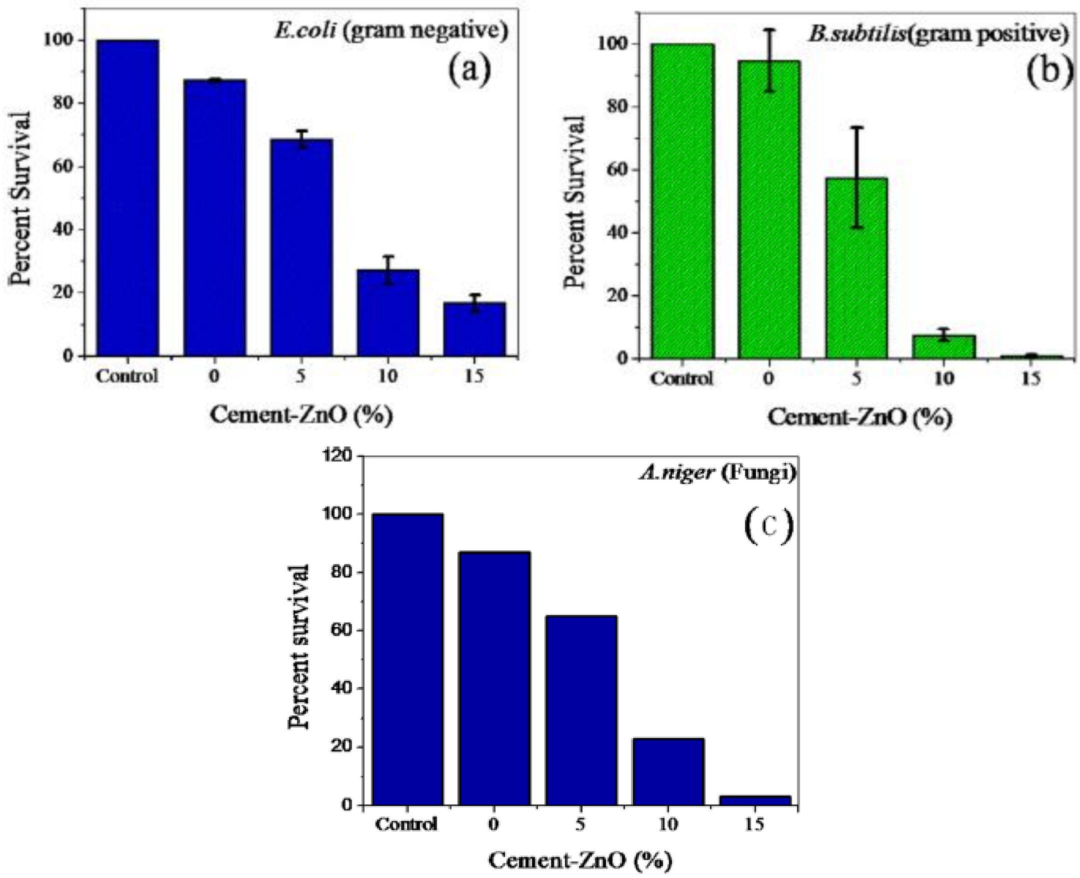


Fig. 5 Effect of different concentrations of cement-ZnO composite on various microorganisms [47]: (a) E. coli, (b) Bacillus subtilis and (c) Aspergillus niger.

Besides above, researchers have also investigated antimicrobial effects of antimicrobial concrete towards some other commonly microbes threatening concrete. For example, Umar et al. [36] evaluated the antimicrobial activity of four types of semi-circular modified cement composite specimens using Serratia marcescens collected from seashore and then isolated from microbe samples. The results showed that cement composites admixed with sodium nitrite-based inhibitor performed better with the least percentage increment of total viable count at the end of 144 h as compared to the cement composite with styrene acrylate copolymer, with acrylic polymer, and cement composite without any admixture, respectively. This can infer that cement composite with sodium nitrite-based inhibitor exhibited noticeably improved ability to suppress the growth of Serratia marcescens in marine environment. NORGANIX [73] is able to endue concrete with powerful antimicrobial property to eliminate Salmonella, Listeria, E. coli, Clostridium, and mold spores not just on the surface but deep within the concrete. Moreover, antimicrobial concrete with NORGANIX can prevent microbes from re-entering concrete from any directions because NORGANIX will hydrate with the unused Portland cement within the concrete to generate new cement, thereby sealing the capillary system. Paiva et al. [20] determined the antimicrobial efficiency of BioSealed for Concrete™, a hydro-silicate catalyst in a colloidal liquid base, to prevent Salmonella spp. attached on concrete bricks in food industry. They found that concrete bricks treated with BioSealed for Concrete™ after inoculation, before and after inoculation had immediate bactericidal effects towards the tested five strains of Salmonella in contrast with bricks not treated with BioSealed for Concrete™ and bricks treated with BioSealed for Concrete™ before inoculation, as observed by significantly lower viable counts of Salmonella.

4.1.2 Antimicrobial concrete with organic antimicrobial agents

Yamanaka at al. [38] studied the inhibitory effects of formats on the growth of bacteria causing concrete corrosion in sewerage systems. They found that the growth of SOB isolated from corroded concrete were completely inhibited by 10 mM calcium formate for 18 days, while the growth of acidophilic iron-oxidizing bacteria was inhibited by 10 mM calcium formate during 34 days. This finding shows that even the same antimicrobial agent has different inhibitory effect on different microbes. In addition, they also observed that the formation of ATP in bacterial cells was ceased after the addition of calcium formate into concrete test pieces. Erbektas et al. [57] evaluated the antimicrobial efficacy of silane quaternary ammonium chloride (SQA) aqueous salt solution against planktonic Halothiobacillus Neapolitanus and A.thiooxidans. They found that the antimicrobial efficacy directly related to bacterial population and activity, and indirectly depends on pH. Furthermore, antimicrobial effectiveness occurs when the pH is greater than 4. In the research undertaken by Do et al. [59], cement mortars with isothiazoline/cabamate exhibited a good antifungal effect against Aspergillus niger, while mortars with nitrofuran did not show inhibitory effect even the content of nitrofuran was up to 5 wt.%. Moreover, the antifungal effect of cement mortar containing isothiazoline/cabamate on Aspergillus niger enhanced almost linearly as the content increases (0%,0.3%,0.5%,1%,2% and 5% by mass to cement). According to [74], researchers of former Soviet Union tested mortar samples with alkyl nitro-bromide (A Ⅱ B) stored for 6 years. The results indicated that the microbial retention rate on the surface of mortar specimens was merely 0.6% and 0.1% when the content of A II B is 0.025 wt.% and 0.05 wt.%, respectively, after 5 hours of irradiation, confirming the strong and long-lasting antimicrobial ability of A II B.

It is worthwhile noting that some organic antimicrobial agents are extremely suitable to add into concrete due to their antimicrobial power to combat against diverse microbes, rather than only a single type of microbe. For example, Kong et al. [62] found that concrete added with copper phthalocyanine exhibited outstanding antimicrobial effect with high bactericidal rates towards Bacteroidetes (90.82%) and Proteobacteria (64.25%), and the bactericidal rate towards all tested microbes is as high as 82.59%. The number of live cells within the biofilm attached to concrete added with copper phthalocyanine showed a significant drop, and the content of live cells was only 12% of that attached to plain concrete. A large number of dead microbes was observed, as seen in Fig. 3 (f). Vaquero et al. [16] studied the bactericidal ability of 15 commercial bactericides blended into concrete against microbial induced corrosion by culturing microbes and evaluating the antimicrobial efficiency. Research results indicated that the multicomponent formulation PL-UV-H-2 B was the sole formulation to succeed in all the evaluation process among all formulations. Concrete samples fabricated with PL-UV-H-2 B, of which the actives are 30% 2-octyl-2H-isothiazol-3-one + Terbutryn and 15% 2,4,4'-trichloro-2'-hydroxy-diphenyl ether (calcium filler as a dispersive matrix), exhibited high effectiveness in antimicrobial tests against algae (Scenedesmus vaculatus and Stichococcus bacillaris), fungus (Aspergillus niger), and bacteria (S. aureus and E.coli), both before and after accelerated aging processes, as exhibited in Fig 6. They also paid special attention to the reasons responsible for failure of some biocide formulations and concluded that the water-soluble bactericide showed a lower retention rate in concrete and thus plays a poor role in protecting concrete in the long term [16]. Urzìet al. [45] evaluated the efficiency of three water-repellent compounds and two biocide compounds, i.e. ALGOPHASE and the new water miscible formulation ALGOPHASE PH 025/d having the same active ingredient 2,3,5,6-tetrachloro-4-methylsulfonyl-pyridine, against microbial colonization of mortars both in laboratory conditions and outdoors. They observed that the application of water-repellent alone was insufficient to prevent biofilm growth on the surface, whereas the combined application of water repellents and biocides in a single step prevent microbial growth, reflecting by complete absence of bacterial colonization, absence of algal colonization, dramatically reduced colonization by fungi on the surface of mortars (seen the representative samples T4 and T5 shown in Fig. 7). Single-step application of biocide and water repellent exhibits excellent performance due to biocide compound randomly distribute below, between and above the hydro-repellent film. In this way, the biocide has the ability to remove the remains of old colonization below, and stop new microbial colonization on the surface [45]. Shook and Bell [37] evaluated the antimicrobial effect of ConShield using wafers of concrete mortar incubated with a bacterial suspension of T.thiooxidans, T. thioparus, and T. denitrificans. The results indicated that the viable bacterial count of concrete wafers treated with ConShield is zero, suggesting that ConShield killed all of the tested bacteria with a complete 100% kill after 24 hours. Moreover, it is reported that ConBlock MIC [75], whether integrated throughout the matrix of concrete when used as an admixture and/or directly applied to concrete as a surface treatment, it inhibits the growth of bacteria, fungi, mold, and algae. Freed et al. [56] evaluated the efficacy of concrete reinforced with fibers incorporating Microban B. The inhibition zone of concrete treated with polypropylene fibers containing Microban B towards E. coli, S. aureus, and mixed mold(fungi) was 3,4, and 2 mm, respectively, indicating fibers carrying Microban B could kill microorganisms.

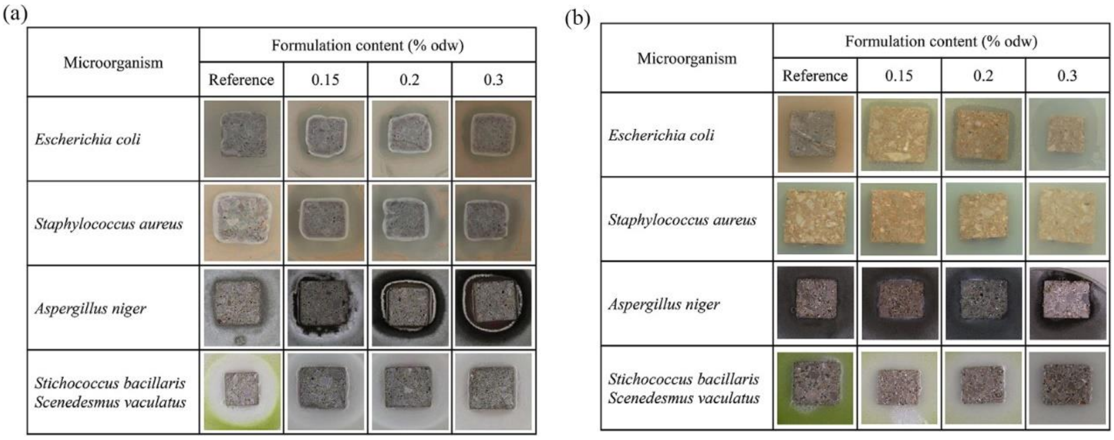


Fig. 6 Effectiveness of concrete incorporated with PL-UV-H-2 B formulation against different microorganisms: (a) before and (b) after the accelerated aging process [16].

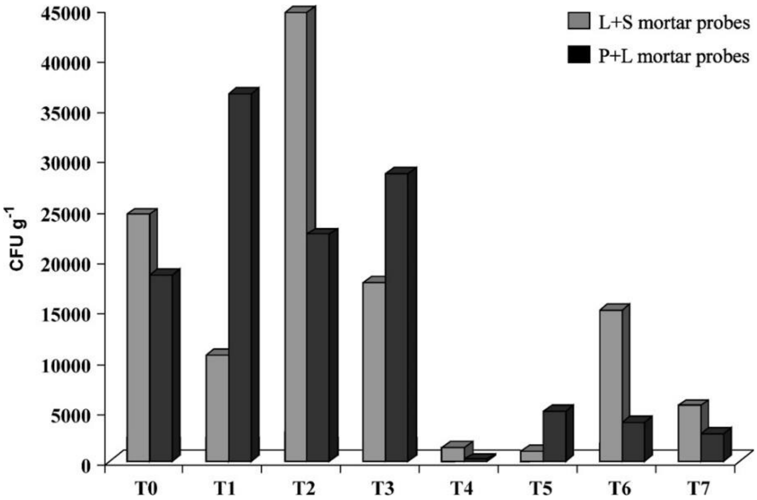


Fig. 7 Enumeration of fungi (CFU g^{-1}) colonizing mortar probes after 15 months of outdoor exposure. L +S=lime +sand and P +L=Pozzolana +lime. T0 represents untreated mortars; T1, T2, T3 represents mortar samples treated with different water-repellent alone; T4, T5, T6 represents mortar probes treated both with water-repellent and biocide; T7 represents mortar probes treated with biocide alone. T4, T5, and T7 treated with ALGOPHASE, and T6 treated with ALGOPHASE PH 025/d [45].

Above investigations have indicated that antimicrobial agents could endow concrete with antimicrobial property to varying degrees. Antimicrobial properties of antimicrobial concrete is largely depending on respective intrinsic natures, types and contents of antimicrobial agents. However, the existing researchers paid little attention to the impact of the addition of antimicrobial agents on the microstructure of concrete. It is necessary to establish the underlying connections between different properties as well as the microstructure of concrete after adding antimicrobial agents. Moreover, high retention rate of antimicrobial agents in concrete is required in order to maintain the long-lasting inhibitory or killing effect towards microbes, while the long-term retention rate of a biocide and its influence on the other properties of concrete are poorly understood [35, 65].

4.2 Mechanical properties

Antimicrobial concrete exhibited different mechanical properties for various types and quantities of antimicrobial agents added. Kim et al. [61] reported that compressive strength of concrete with antimicrobial watertight admixture, of which antimicrobial ingredients are nickel and tungsten compounds, was decreased at an early age but the long-term compressive strength was increased. De Muynck et al. [25] observed a small decrease in compressive strength of mortar specimens added with the highest concentration of zeolites (4.65%), i.e. 41.1± 0.8 MPa as compared to 49.0±3.4 MPa for control specimens. Kong and Zhang et al. [65,76] tested the 7 days, 28 days and 56 days compressive strength of concrete added with different types and contents of bactericide. They observed that the 28 days compressive strength of concrete adding with copper phthalocyanine (CP) was enhanced by 60% with the dosage of 0.1%, which indicated that CP not only increased the fluidity of concrete, but also accelerated the hydration of cement, thus promoted the strength development by dispersing cement. Meanwhile, the enhancement of compressive strength also makes some contribution to maintain the surface pH of concrete added CP as high as 10.6. However, the strength of concrete will be impaired when the contents of zinc oxide and dodecyl dimethyl benzyl ammonium added in concrete are more than 0.05% [65,76]. Umar et al. [36] investigated the strength development of four types of cement composite modified with polymer/added inhibitor at the age of 7, 21, and 28 days. The results showed that compressive strength of cement composite admixed with sodium nitrite-based inhibitor is increased by 26% (28 days) with respect to that of cement composite without any admixture, and higher than cement composite prepared with styrene acrylate copolymer and acrylic polymer, as shown in Fig. 8. Vaquero et al. [16] obtained that the 28 d compressive strength of concrete mixed with multicomponent formulation PL-UV-H-2 B was 37.1, 36.9, 35.7, and 34.9 MPa when the content is 0, 0.15, 0.2, and 0.3%, respectively, and the 28 d flexural strength was 9.4, 8.6, 8.2, and 8.5 MPa when the content is 0, 0.15, 0.2, and 0.3%, respectively. Consequently, they concluded that the addition of PL-UV-H-2 B in concrete only slightly decreased the compressive strength and flexural strength as compared to those of control samples [16]. Moreover, Do et al. [59] observed that compressive and flexural strengths of cement mortar containing the antifungal agent of isothiazoline/cabamate were almost equal to those of non-added cement mortar; hence, they concluded that the addition of isothiazoline/cabamate has a very little adverse impact on compressive and flexural strengths of cement mortar and is negligibly insignificant.

4.3 Mass/weight loss

Researchers not only investigated the antimicrobial and mechanical properties of antimicrobial concrete, but also paid attention to its mass/weight loss. For example, Negishi et al. [41] obtained that the weight loss of cement specimens without antimicrobial agents, with 0.075% metal nickel, and with 0.075% metal nickel plus 0.075% calcium tungstate was 10, 6, and 1%, respectively, after being exposed to a sewage treatment plant containing 28 ppm of H_2S for 2 years. The least weight loss of nickel modified samples after adding calcium tungstate was due to the higher binding tendency of tungsten to A. thiooxidans. As it can be seen in Fig. 9, there is an apparent difference in mass losses in specimens with various bactericides and without adding any bactericide, the mass loss rate of concrete specimen with copper phthalocyanine was the lowest (4.78%) as compared to other specimens, providing evidence that copper phthalocyanine has the best effect on resistance to the microbial induced corrosion of concrete [62]. Bao [67] reported that the mass loss of reference mortars and mortars added with mineral powder and fly ash was 1.26, 0.44 and 0.47% after an immersion in intensified sewage for 5 months, respectively. While the mass loss of mortar samples with antimicrobial agent sodium tungstate and sodium bromide reached 0.57% and 0.6%, which indicated that incorporation of admixture has a better improvement effect than antimicrobial agents from the perspective of reduced mass loss. In addition, Shook and Bell [37] conducted an in-situ field test using concrete samples from concrete pipe in a sewer manhole which had evident corrosion occurring and an obviously high H_2S concentration. They obtained that concrete samples treated without ConShield had a great weight loss of 3.44%, whereas the concrete samples treated with ConShield showed a significantly lower weight loss of 0.32% after 3 months.

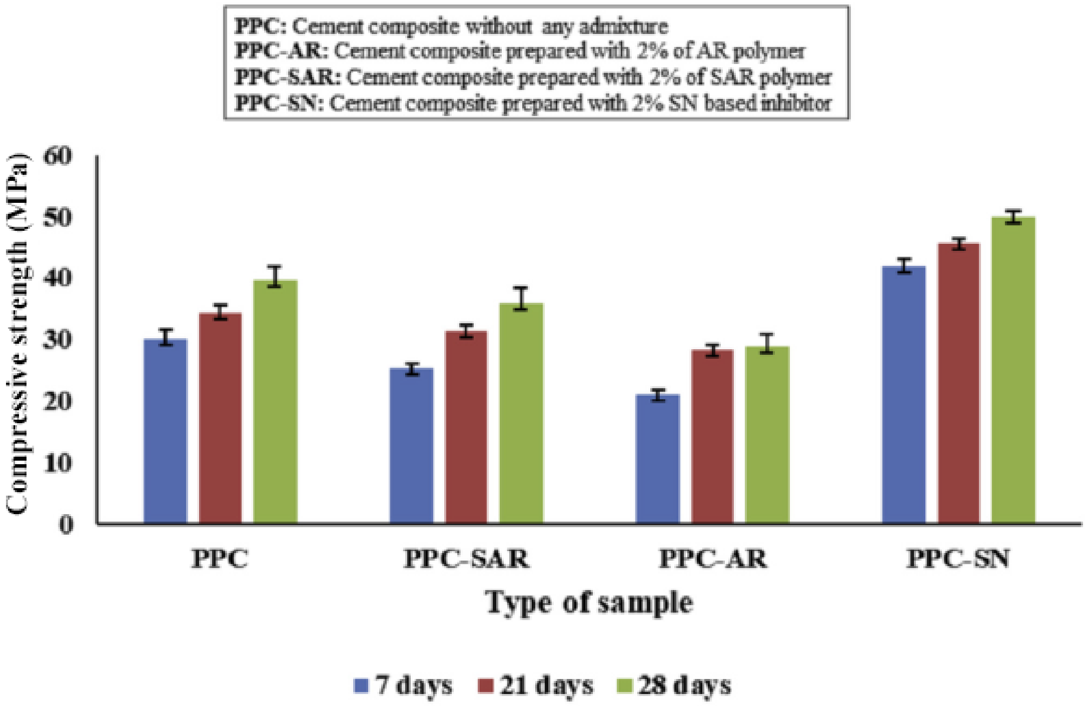


Fig. 8 Comparison of compressive strength of (SAR denotes styrene acrylate copolymer, AR denotes acrylic polymer and SN denotes sodium nitrite) [36].

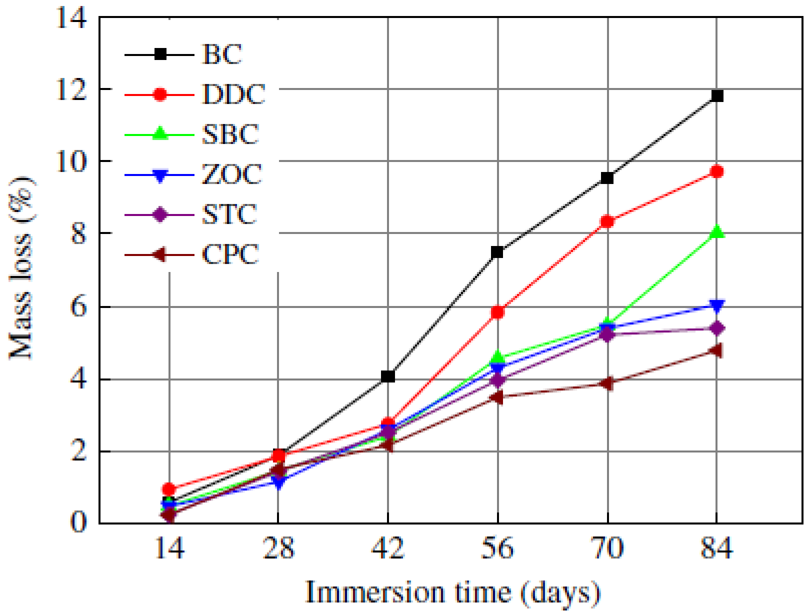


Fig. 9 Effect of various bactericides on mass loss of concrete immersed in sewage [62]. DDC, SBC, ZOC, STC, CPC, and BC represent concrete incorporated with dodecyl dimethyl benzyl ammonium chloride, sodium bromide, zinc oxide, sodium tungstate, copper phthalocyanine, and plain concrete without bactericide, respectively.

5. Antimicrobial mechanisms of antimicrobial agents

5.1 Antimicrobial mechanisms of inorganic antimicrobial agents

The antimicrobial mechanisms of heavy metal antibacterial agents towards microorganisms attached to and/or penetrated into concrete is generally considered to follow the reactions below. During the action of antibacterial agents, metal ions gradually dissolve and react with thiol group (-SH), amino group (-NH_2) and other sulfur nitrogen-containing functional groups existing in proteins and nucleic acids of bacteria, which inhibit or inactivate some necessary enzymes, and disturb the osmotic stability of the cell, thus achieving the antibacterial purpose [34,51,77]. More specifically, the action of silver ion released from the zeolite matrix in concrete and reactive oxygen species (ROS) generated from silver within the matrix are considered as the mechanisms of bactericidal action of silver-loaded zeolites, and it has been reported that either the silver itself or the ROS must interact with biological macromolecules like enzymes and DNA by an electron release mechanism to maintain long-lasting antibacterial effect [63, 70]. It is assumed that nickel does not attack on bacteria themselves, but binds to an enzyme of bacteria to exhibit growth inhibitory effect [43]. Nogami et al. [39] concluded that nickel ions incorporated into concrete bind to the plasma membrane and inhibit the activity of sulfur dioxygenase and sulfite oxidase of T. thiooxidans to exert its inhibitory effect. Maeda et al. [40] also stated that nickel binds to T. thiooxidans cells and inhibits enzymes involved in sulfur oxidation of the bacterium, consequently inhibiting cell growth and sulfuric acid generation. Similarly, tungsten exerts its antimicrobial effect on A. thiooxidans by binding to A. thiooxidans cells and inhibiting the sulfur oxidation enzyme system, such as sulfur oxidase, sulfur dioxygenase and sulfite oxidase of cells [41]. Sugio et al. [42] also studied the mechanism of growth inhibition by tungsten in A. ferrooxidans, concluding that tungsten binds to cytochrome c oxidase in plasma membranes and inhibits cytochrome c oxidase activity, stopping cell growth from oxidation of Fe^{2+}. Moreover, Kim et al. [61] ascribed the antimicrobial mechanism of antimicrobial metals (Ni and W) to the destruction of cell membrane or internal protein tissue of microbe by Ni and W according to simulation tests.

Significantly increased surface area-to-volume ratio of nanoparticles contributes to greater interaction with microorganisms and enhances the release of toxic ions, assisting nanoparticles to achieve excellent antimicrobial properties [3,78]. The multiple bactericidal mechanisms of nanomaterials, such as copper oxide and zinc oxide nanoparticles, have been attributed to damage of the cell membrane by either direct contact with nanoparticles or photocatalytic production of ROS; release of toxic ions; interruption of electron transport, protein oxidation, and modification of membrane charges. Degradation of DNA, RNA and proteins by ROS, and lowering the production of ATP due to acidification and ROS production also accounts for bactericidal properties of nano-sized materials [3,79]. Fig. 10 illustrates a comparison of antibacterial mechanisms between antimicrobial nanomaterials and their bulk counterparts. In addition, the two major explanations to the photo-sterilization mechanism of concrete involving nano-TiO_2 under light are the attack of chemical species leading to the death of microorganisms or the biological structure destruction causing the inactivation of microorganisms [55].

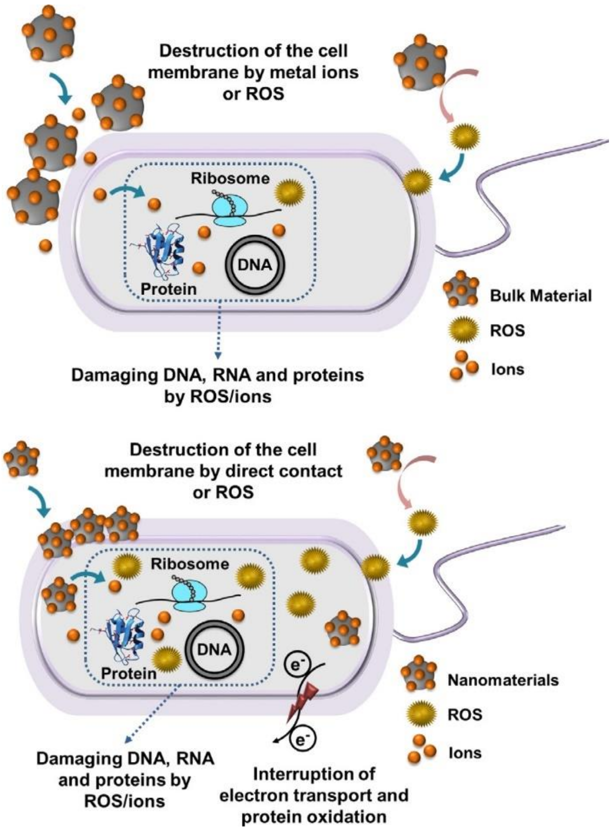


Fig. 10 Illustration of possible bactericidal mechanism of nanomaterials (bottom) compared to their bulk form (top) [3].

5.2 Antimicrobial mechanisms of organic antimicrobial agents

Generally, organic antimicrobial agents inhibit the growth and reproduction of microorganisms by destroying cell membranes, denaturing proteins, or disrupting metabolic processes. The phthalocyanine compound contained in concrete or mortar can be easily introduced into the cell of SOB, inhibiting enzyme reaction within the cell and, eventually, killing SOB [11]. In terms of copper phthalocyanine [62,65,76], its high bactericidal property towards bacteria is mainly provided by copper ions. Copper ions could interfere with the metabolic process of bacterial cells or interfere with the function of various enzymes, losing their biological functions and eventually leading to the death of cells [62,65,76]. Quats, like dodecyl dimethyl benzyl ammonium chloride [62,65], the positively charged organic cations can be selectively adsorbed by the negatively charged bacteria contacting with concrete. They could enter into the cell membrane by permeation and diffusion, thus impede the semi-permeation action of cell membranes and then inhibit the generation of enzyme to achieve the sterilization effect [80]. McDonnel et al. [81] proposed that Quats target the cytoplasmic membrane and damage the phospholipid bilayer. Additionally, the cellular membrane of bacteria will be pierced by the long molecular carbon chain of silane quaternary ammonium chloride (SQA) [57] and cell destruction will be triggered by ions exchange between the positively charged ammonium cation of SQA and ions within cell membranes, are two major hypotheses accounting for the antimicrobial working mechanisms of SQA. The antimicrobial mechanism of concrete with ConBlock MIC [75] is the active ingredient in ConBlock MIC 3-Trimethoxy silyl propyl dimethyl octadecyl ammonium chloride has a positive charged nitrogen atom (as shown in Fig. 11), electrostatically attracting many bacteria to the molecule. The molecular chain of carbon 18 atoms long pierces the cellular membrane of bacteria and the outer cell is punctured upon reaching the nitrogen atom. Consequently, it creates an uninhabitable environment for the microbiological organisms on the surface of concrete [75]. As for ConShield, it endues concrete with excellent antimicrobial effect through molecularly bonding to the ingredients of concrete mix, then, providing hundreds of microscopic spikes over an area of a single bacterium, which puncture the fragile single cell of bacteria [82, 83].

However, majority of the antimicrobial mechanisms mentioned above are relevant to inhibiting or killing bacteria, the antifungal and algaecidal mechanisms of corresponding antimicrobial agents used in concrete are rare, requiring further investigations.

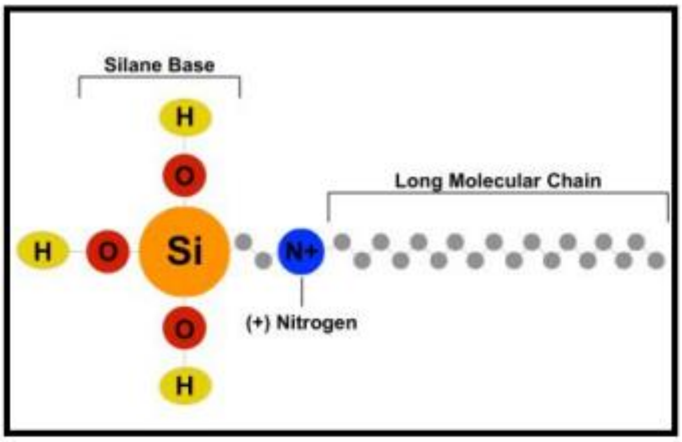


Fig. 11 Molecular structure of 3-Trimethoxy silyl propyl dimethyl octadecyl ammonium chloride [75].

6. Applications of antimicrobial concrete

Concrete is the most abundant material in wastewater systems but at the greatest risk for corrosion. Despite most of the findings are based upon laboratory testing, there still exist some findings from practical applications of antimicrobial concrete. Considering the superior antimicrobial property of concrete imparted by some typical antimicrobial agents, one of the major applications of antimicrobial concrete is to mitigate and control microbial corrosion caused by microbial metabolism in sewer systems, such as concrete sewage pipes, sewer manholes, wastewater collection systems and treatment plants, etc. For instance, in order to combat the growth and proliferation of Thiobacilli in sewer systems, new sewer construction in Atlanta has been utilizing concrete admixed with ConShield since 1997, and rehabilitation works of concrete manholes in Columbus, OH, Oskaloosa Co., FL, Mt. Prospect, IL, Miami, FL, and Corsica, TX have adopted the same material [37]. The results shown in Fig. 12 (a) and (b) clearly demonstrated the long-term protection due to the addition of

ConShield into concrete against microbial induced corrosion in the Maline Drop Shaft [82]. Owing to the proved high antimicrobial effectiveness, ConShield has a wide range of industrial applications in concrete structures mainly including two aspects: one is new and rebuilt concrete structures subjected to highly concentrated sulfide conditions like concrete pipe and manholes (Fig. 12 c),wet wells, lift stations, WWTP head works, clarifiers, and the like. Another one is rehabilitation of heavily corroded manholes, pipelines and tunnels in place via shotcrete (Fig. 12 d) [83]. Similarly, with excellent antimicrobial power and long-lasting antimicrobial effect, concrete incorporated with antimicrobial additive Zeomighty (zeolite-supported silver and copper) was popular in the Japanese market. The practical applications of antimicrobial concrete with Zeomighty include secondary concrete products such as Hume pipes, manholes, and box culverts, cast-in place concrete structures for sewer and treatment facilities and other premix mortar, etc., as shown in Fig. 13 [33]. Kurihara et al. [84] invented an antibacterial agent composed of a silver compound (selected from silver carbonate, silver oxide and silver phosphate), a copper compound (selected from copper carbonate, copper oxide, copper phosphate and copper hydroxide) and an ion-retaining compound, and concrete containing the antibacterial agent exhibits outstanding antibacterial effect against SRB, SOB, and carboxylic acid-producing bacteria particularly in sewage treatment plants. Uchida et al. [11] disclosed that the addition of phthalocyanine compound (a metal phthalocyanine, a metal-free phthalocyanine, and derivatives thereof) in concrete or mortar can be easily introduced into a cell of SOB, thus inhibit and/or kill SOB via inhibiting enzyme reaction within the cell of SOB. Consequently, the deterioration inhibitor with the effective component, phthalocyanine compound, showed ability to mitigate the deterioration of concrete or mortar. Antimicrobial concrete fabricated with copper phthalocyanine [62,65] has the merits of excellent bactericidal performance, high retention rate of bactericide and low cost. Moreover, the addition of copper phthalocyanine does not affect the performance of concrete. Consequently, such antimicrobial concrete can be widely used in the construction of municipal sewage facilities [85]. Moreover, it is stated that the antimicrobial additive ConBlock MIC can be applied in new concrete infrastructure and cementitious infrastructure repair products, for example, concrete pipe, manhole and septic tanks, or for ready mixed concrete or cementitious mortars and liners [75]. With the advantages of long-lasting bactericidal effect on SOB (one to several years), the low cost and environmentally friendly chemical (i.e. nitrite), FNA spray [44] is a promising practical technology for mitigate and control of microbially induced concrete corrosion.

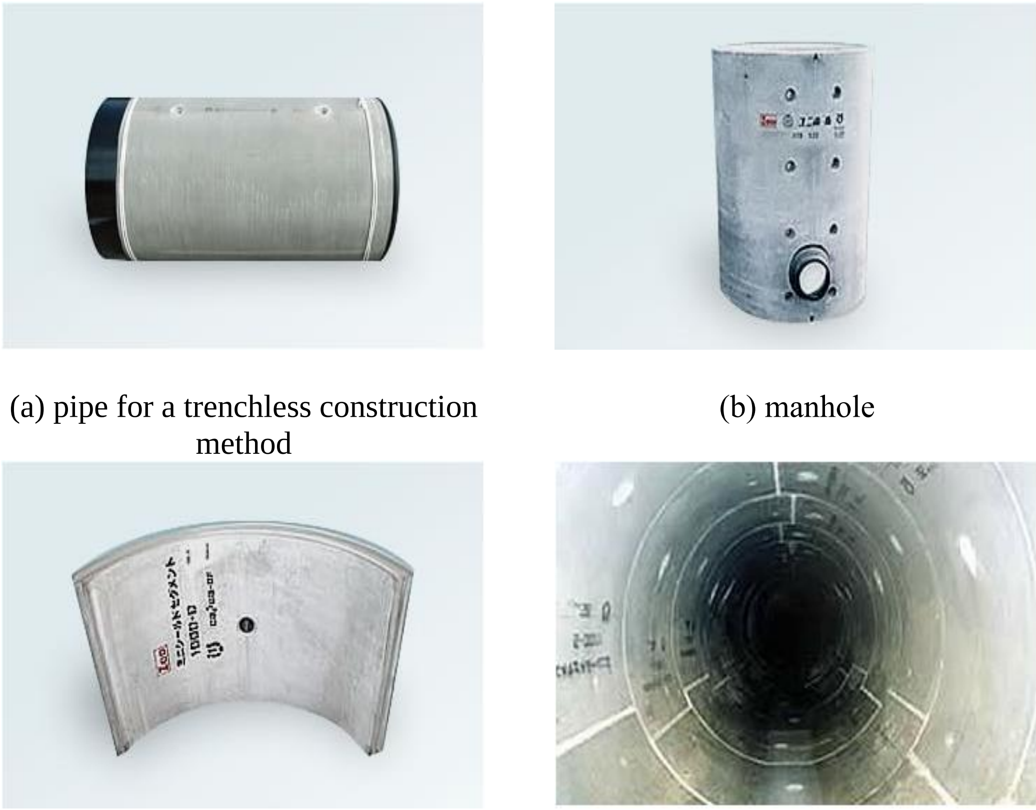
(a) Corrosion prior to repair in 1999

(b) Shaft after repair in 2009

(c) New concrete pipe and manholes with ConShield precisely metered into the mix at the plant

(d) Rehabilitation of pipelines and tunnels in place by shotcrete added with ConShield

Fig. 12 Comparison before (a) and after (b) adding ConShield of the Maline Drop Shaft [82], and (c) and (d) are the examples of industrial use of ConShield [83].



(a) pipe for a trenchless construction method

(b) manhole

(c) mini-shield segment before construction execution

(d) mini-shield segment after construction execution

Fig. 13 Examples of actual applications of antimicrobial concrete with Zeomighty [33].

In addition, according to [86], concrete added with copper oxide (methyl cellulose as dispersant) and zinc oxide (fly ash as dispersant) was proved to be able to protect marine ecological engineering construction from microorganism attack. Compared to the untreated concrete columns with a number of plaques found on the surface, no evidence of plaque was found on the surface of three treated concrete columns after 18 months. Similarly, concrete with TiO_2, utilizing the light-induced bactericidal activity of TiO_2, can be employed to control microbiological growth on concrete surfaces, thus enhancing the durability of concrete in ocean engineering. The same concrete can be also used as exterior wall materials of buildings, achieving sterilization function by decomposing bacteria attached on surface [49, 87]. Janus et al. [88] proposed that concretes admixed with modified titania, with enhanced antibacterial properties, can have a wide application in places demanding high sterilization levels, such as hospitals, institutions, school and water storage tanks. In addition, Freed et al. [56] disclosed that antimicrobial concrete reinforced with fiber carrying antimicrobial agents, such as Microban B, has the ability to protect concrete from biological attack. The antimicrobial agent is first incorporated into or coated onto fibers and then the treated fibers are admixed with concrete. Such antimicrobial concrete, with the ability to inhibit growth and contact of microorganisms such as bacteria, fungi, mold, etc., aims to be employed in areas requiring extraordinary cleanliness such as food processing plants, hospitals, kitchens, locker rooms, and the like.

7. Summary and prospects

Microbial attachment, colonization and eventually deterioration have been a great threat to concrete structures in sewer systems, marine environments, buildings exposed to high humidity and the like. Antimicrobial concrete, with the addition of inorganic or organic antimicrobial agents, exhibits excellent antimicrobial effect against specific microorganism and helps to address such issues caused by microorganism metabolism. Also, the appearance of antimicrobial concrete makes infrastructures smarter and more durable, prolongs the service life of infrastructures and lowers the huge cost by rehabilitation and even replacement.

Despite many investigations have been conducted in this area in the past decades, there still remains some key issues to be addressed. The relationship between antimicrobial property and various affecting parameters (including contents, retention rate and dispersion, etc.) should be further comprehensively investigated so as to effectively enhance the antimicrobial effect of antimicrobial concrete. Combining different antimicrobial agents to form biocide formulation according to their respective intrinsic properties may be a promising strategy to boost antimicrobial efficiency. The toxicity due to the release of some active ingredients into the environment during the entire service life of inorganic antimicrobial agents such as nanoparticles and generally temporary effectiveness for organic antimicrobial agents are impediments to the widespread application of antimicrobial concrete. Moreover, the resistance of microorganisms to antimicrobial agents has to be considered in developing antimicrobial concrete.

Currently, most researches are restricted to the laboratory stage, practical applications are few and field trails are still highly required to verify the feasibility of antimicrobial concrete with aforementioned antimicrobial agents. The development of antimicrobial concrete is based on the advancement of antimicrobial agents. In future, it is expected to provide novel, high-efficiency, long lasting, broad-spectrum and environmental-friendly antimicrobial agents for fabricating antimicrobial concrete. In addition, antimicrobial concrete with its exceptional antimicrobial performance may have an extended application in the field of fighting against viruses. Especially, the world is in novel coronavirus pandemic now. Countries around the world are building new hospitals or improving the facilities of existing hospitals to better treat infected patients. Additionally, following its detection in the sewers in Massachusetts, the novel coronavirus was also reported to be found in the non-potable water system used for cleaning streets and watering parks in Paris. If the infrastructures such as hospitals and sewage systems have the ability to kill viruses, it is beneficial for preventing the spread and reproduction of viruses. Furthermore, the combination of new technologies may promote the development of antimicrobial concrete, such as nanotechnology, geopolymer technology, 3D printing/digital production technology, biotechnology, self-assembly technology, damage and failure evaluation technology, organic-inorganic composite technology and multiscale simulation technology [89-100].

Acknowledgments

The authors thank the funding supported from the National Science Foundation of China (51908103 and 51978127), and the China Postdoctoral Science Foundation (2019M651116).

References

[1]. Nica D, Davis JL, Kirby L, Zuo G, Roberts DJ. Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers. International Biodeterioration and Biodegradation, 2000,46(1):61-68.

[2]. Wang YM and Meng YF. Reviewed of antibacterial concrete research and application status. Ningxia Engineering Technology, 2016,15(1):93-96.

[3]. Noeiaghaei T, Mukherjee A, Dhami N, Chae SR. Biogenic deterioration of concrete and its mitigation technologies. Construction and Building Materials, 2017, 149:575-586.

[4]. Vishwakarma V, Sudha U, Ramachandran D, Anandkumar B, George RP, Kumari K, Preetha R, Kamachi Mudali U, Pillai CS. Enhancing antimicrobial properties of fly ash mortars specimens through nanophase modification. Materials Today: Proceedings, 2016,3(6):1389-1397.

[5]. Islander RL, Devinny JS, Mansfeld F, Postyn A, Shih H. Microbial ecology of crown corrosion in sewers. Journal of Environmental Engineering, 1991,117(6):751-770.

[6]. Mori T, Nonaka T, Tazaki K, Koga M, Hikosaka Y, Noda S. Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes. Water

Research, 1992,26(1):29-37.

[7]. Parker CD. Mechanics of corrosion of concrete sewers by hydrogen sulfide. Sewage and Industrial Wastes, 1951:1477-1485.

[8]. Wei S, Jiang ZL, Liu H, Zhou DS, Sanchez Silva M. Microbiologically induced deterioration of concrete: a review. Brazilian Journal of Microbiology, 2013,44(4):1001-1007.

[9]. Parker CD. The corrosion of concrete: 1. The isolation of a species of bacterium associated with the corrosion of concrete exposed to atmospheres containing hydrogen sulphide. Australian Journal of Experimental Biology and Medical Science, 1945,23(2):81-90.

[10]. Satoh H, Odagiri M, Ito T, Okabe S. Microbial community structures and in situ sulfate-reducing and sulfur-oxidizing activities in biofilms developed on mortar specimens in a corroded sewer system. Water Research, 2009,43(18):4729-4739.

[11]. Uchida H, Enokida T, Tanaka R, Tamano M. Deterioration preventive for concrete or mortar and method for preventing deterioration of concrete or mortar. Patent US 6159281,2000.

[12]. Cho, KS and Mori T. A newly isolated fungus participates in the corrosion of concrete sewer pipes. Water Science and Technology, 1995,31(7):263-271.

[13]. Gu JD, Ford TE, Berke NS, Mitchell R. Biodeterioration of concrete by the fungus Fusarium. International Biodeterioration and Biodegradation, 1998,41(2):101-109.

[14]. Lv JF and Ba HJ, Splash zone concrete of marine concrete engineering by SEM and surface microorganism identification by 16S rRNA. Journal of Wuhan University of Technology, 2009,31(2):28-32.

[15]. Lv JF, Li J, Mo ZL, Ba HJ. Microorganism identification by 16S rDNA of concrete surface exposed to a tidal zone. Journal of Harbin Engineering University,

2010,31(10):1386-1392.

[16]. Vaquero JM, Cugat V, Segura I, Calvo MA, Aguado A. Development and experimental validation of an overlay mortar with biocide activity. Cement and Concrete Composites, 2016,74:109-119.

[17]. Le JX, Yan YN, Li XY, Gao PW. Corrosion mechanism and control technology of microorganism participation in concrete. Jiangsu Building Materials, 2006, (3):14-17.

[18]. Fonseca AJ, Pina F, Macedo MF, Leal N, Romanowska-Deskins A, Laiz L, Gomez-Bolea A, Saiz-Jimenez C. Anatase as an alternative application for preventing biodeterioration of mortars: evaluation and comparison with other biocides. International Biodeterioration and Biodegradation, 2010,64(5):388-396.

[19]. Alum A, Rashid A, Mobasher B, Abbaszadegan M. Cement-based biocide coatings for controlling algal growth in water distribution canals. Cement and Concrete Composites, 2008,30(9):839-847.

[20]. Paiva DM, Singh M, Macklin KS, Price SB, Hess JB, Conner DE. Antimicrobial activity of commercial concrete sealant against Salmonella spp: A model for poultry processing plants. International Journal of Poultry Science, 2009,8(10):939-945.

[21]. Xie YD, Lin XJ, Ji T, Liang YG, Pan WJ. Comparison of corrosion resistance mechanism between ordinary Portland concrete and alkali-activated concrete subjected to biogenic sulfuric acid attack. Construction and Building Materials, 2019,228:117071.

[22]. Zhang D. Study on anti-bacteria concrete. New Building Materials, 2002, (4):13-14.

[23]. Zhang XW, Zhang X. Present and prospect of microbial corrosion prevention of concrete. Materials Protection, 2005, (11):44-48.

[24]. Rivera-Garza M, Olguin MT, Garcia-Sosa I, Alcantara D, Rodriguez-Fuentes G.

Silver supported on natural Mexican zeolite as an antibacterial material. Microporous and Mesoporous Materials, 2000,39(3):431-444.

[25]. De Muynck W, De Belie N, Verstraete W. Antimicrobial mortar surfaces for the improvement of hygienic conditions. Journal of Applied Microbiology, 2010,108(1):62-72.

[26]. Haile T, Nakhla G, Allouche E, Vaidya S. Evaluation of the bactericidal characteristics of nano-copper oxide or functionalized zeolite coating for bio-corrosion control in concrete sewer pipes. Corrosion Science, 2010,52(1):45-53.

[27]. Dutta P and Wang B. Zeolite-supported silver as antimicrobial agents. Coordination Chemistry Reviews, 2019,383: 1-29.

[28]. Haile T, Nakhla G, Allouche E. Evaluation of the resistance of mortars coated with silver bearing zeolite to bacterial-induced corrosion. Corrosion Science, 2008,50(3):713-720.

[29]. Haile T and Nakhla G. Inhibition of microbial concrete corrosion by Acidithiobacillus thiooxidans with functionalized zeolite-A coating. Biofouling, 2009, 25(1):1-12.

[30]. Haile T and Nakhla G. The inhibitory effect of antimicrobial zeolite on the biofilm of Acidithiobacillus thiooxidans. Biodegradation, 2010,21(1):123-134.

[31]. Xu AZ. Experimental Research on new type antibacterial high-performance concrete. Master Thesis, Ningxia University, China, 2014.

[32]. Li CP. The antibacterial experiment study based on durability of concrete. Master Thesis, Ningxia University, China, 2015.

[33].http://www.zeomic.co.jp/en/product/antimicrobial_concrete_additive_zeomighty/index.html

[34]. Cloete TE. Resistance mechanisms of bacteria to antimicrobial compounds.

International Biodeterioration and Biodegradation, 2003,51(4):277-282.

[35]. Zhang XW, Zhang X. Mechanism and research approach of microbial corrosion of concrete. Journal of Building Materials, 2006,9(1):52-58.

[36]. Umar M, Fathima N, Haji Sheik Mohammed MS, Hemalatha S. Modified cement composites for protection against microbial induced concrete corrosion of marine structures. Biocatalysis and Agricultural Biotechnology, 2019,20:101192.

[37]. Shook WE and Bell LW. Corrosion control in concrete pipe and manholes. In: Proc., Int. Conf. Water Environment federation, Orlando, Fa. 1998.

[38]. Yamanaka T, Aso I, Togashi S, Tanigawa M, Shoji K, Watanabe T, Watanabe N, Maki K, Suzuki H. Corrosion by bacteria of concrete in sewerage systems and inhibitory effects of formates on their growth. Water Research, 2002,36(10):2636-2642.

[39]. Nogami Y, Maeda T, Negishi A, Sugio T. Inhibition of sulfur oxidizing activity by nickel ion in Thiobacillus thiooxidans NB1-3 isolated from the corroded concrete. Bioscience, Biotechnology, and Biochemistry, 1997,61(8):1373-1375.

[40]. Maeda T, Negishi A, Nogami Y, Sugio T. Nickel inhibition of the growth of a sulfur-oxidizing bacterium isolated from corroded concrete. Bioscience, Biotechnology, and Biochemistry, 1996,60(4):626-629.

[41]. Negishi A, Muraoka T, Maeda T, Takeuchi F, Kanao T, Kamimura K, Sugio T. Growth inhibition by tungsten in the sulfur-oxidizing bacterium Acidithiobacillus thiooxidans. Bioscience, Biotechnology, and Biochemistry, 2005,69(11):2073-2080.

[42]. Sugio T, Kuwano H, Negishi A, Maeda T, Takeuchi F, Kamimura K. Mechanism of growth inhibition by tungsten in Acidithiobacillus ferrooxidans. Bioscience, Biotechnology, and Biochemistry, 2001,65(3):555-562.

[43]. Maeda T, Negishi A, Nogami Y, Sugio T. Thiobacillus thiooxidans growth inhibitor. Patent US 6146666,2000.

[44]. Sun XY, Jiang GG, Bond PL, Keller J, Yuan ZG. A novel and simple treatment for control of sulfide induced sewer concrete corrosion using free nitrous acid. Water Research, 2015,70:279-287.

[45]. Urzì C and De Leo F. Evaluation of the efficiency of water-repellent and biocide compounds against microbial colonization of mortars. International Biodeterioration and Biodegradation, 2007, 60(1):25-34.

[46]. De Muynck W, Ramirez AM, De Belie N, Verstraete W. Evaluation of strategies to prevent algal fouling on white architectural and cellular concrete. International Biodeterioration and Biodegradation, 2009,63(6):679-689.

[47]. Singh VP, Sandeep K, Kushwaha HS, Powar S, Vaish R. Photocatalytic, hydrophobic and antimicrobial characteristics of ZnO nano needle embedded cement composites. Construction and Building Materials, 2018,158:285-294.

[48]. Wang YM. The experimental research on antimicrobial properties of high-performance concrete with nano-zinc oxide. Master Thesis, Ningxia University, China, 2016.

[49]. Li Z, Ding SQ, Yu X, Han BG, Ou JP. Multifunctional cementitious composites modified with nano titanium dioxide: A review. Composites Part A, 2018,111:115-137.

[50]. Ganji N, Allahverdi A, Naeimpoor F, Mahinroosta M. Photocatalytic effect of nano-TiO_2 loaded cement on dye decolorization and Escherichia coli inactivation under UV irradiation. Research on Chemical Intermediates, 2016,42(6):5395-5412.

[51]. Li WG, Lu WP, Wang HB, Huo JC. Progress of antibacterial materials. New Chemical Materials, 2003,31(3):9-12.

[52]. Zhang WZ. The novel inorganic antibacterial agent silver molybdate. New Chemical Materials, 2004,32(3):29-31.

[53]. Ortega-Morales BO, Reyes-Estebanez MM, Gaylarde CC, Camacho-chab JC,

Sanmartin P, Chan-Bacab MJ, Granados-Echegoyen CA, and Pereanez-Sacarias JE. Antimicrobial properties of nanomaterials used to control microbial colonization of stone substrata. Advanced materials for the conservation of stone. Springer, Cham, 2018:277-298.

[54]. Sikora P, Augustyniak A, Cendrowski K, Nawrotek P and Mijowska E. Antimicrobial Activity of Al_2O_3, CuO, Fe_3O_4, and ZnO nanoparticles in scope of their further application in cement-based building materials. Nanomaterials, 2018,8(4):212.

[55]. Vittoriadiamanti M and Pedeferri MP. Concrete, mortar and plaster using titanium dioxide nanoparticles: Applications in pollution control, self-cleaning and photo sterilization. Nanotechnology in Eco-Efficient Construction, 2013:299-326.

[56]. Wayne Freed W, Mountain S, Tenn. Reinforced concrete containing anti-microbial enhanced fibers. Patent US 6162845, 2000.

[57]. Erbektas AR, Isgor OB and Weiss WJ. Evaluating the efficacy of antimicrobial additives against biogenic acidification in simulated wastewater exposure solutions. RILEM Technical Letters, 2019,4:49-56.

[58]. Javaherdashti R and Alasvand K. Chapter 3-An Introduction to Microbial Corrosion. Biological Treatment of Microbial Corrosion, 2019:25-70.

[59]. Do J, Song H, So H, Soh Y. Antifungal effects of cement mortars with two types of organic antifungal agents. Cement and Concrete Research, 2005,35(2):371-376.

[60]. Cai YC. Study on preparation and properties of silver nanocomposites. Doctoral Thesis, Huazhong University of Science and Technology, China, 2017.

[61]. Kim GY, Lee EB, Khil BS, Lee SH. Evaluation of properties of concrete using fluosilicate salts and metal (Ni, W) compounds. Transactions of Nonferrous Metals Society of China, 2009, 19:s134-s142.

[62]. Kong LJ, Zhang B and Fang J. Effect of bactericide on the deterioration of

concrete against sewage. Journal of Materials in Civil Engineering, 2018,30(8):04018160.

[63]. Tang Q, Chen NC. Research and development of zeolite antibacterial agent. China Non-Metallic Industry Guide, 2009,30(4):15-18.

[64]. Xu AZ, Meng YF. Experimental study of antibacterial high-performance concrete. Journal of Green Science and Technology, 2014, (4):315-317.

[65]. Kong LJ, Zhang B and Fang J. Study on the applicability of bactericides to prevent concrete microbial corrosion. Construction and Building Materials, 2017,149:1-8.

[66]. Southerland WM and Toghrol F. Sulfite oxidase activity in Thiobacillus novellus. Journal of bacteriology, 1983,156(2):941-944.

[67]. Bao X. Experimental and prediction study on the deterioration behavior of concrete in municipal sewage. Master Thesis, Shijiazhuang Tiedao University, China, 2016.

[68]. Sikora P, Cendrowski K, Markowska-Szczupak A, Horszczaruk E, Mijowska E. The effects of silica/titania nanocomposite on the mechanical and bactericidal properties of cement mortars. Construction and Building Materials, 2017,150:738-746.

[69]. De Muynck W, De Belie N and Verstraete W. Effectiveness of admixtures, surface treatments and antimicrobial compounds against biogenic sulfuric acid corrosion of concrete. Cement and Concrete Composites, 2009,31(3):163-170.

[70]. Haile T, Nakhla G, Zhu J, Zhang H, Shugg J. Mechanistic study of the bactericidal action of silver-loaded chabasite on Acidithiobacillus thiooxidans. Microporous and Mesoporous Materials, 2010, 127(1-2):32-40.

[71]. Dyshlyuk L, Babich O, Ivanova S, Vasilchenco N, Atuchin V, Korolkov I, Russakov D, Prosekov A. Antimicrobial potential of ZnO, TiO_2 and SiO_2 nanoparticles in protecting building materials from biodegradation. International Biodeterioration

and Biodegradation, 2020,146:104821.

[72]. Linkous CA, Carter GJ, Locuson DB, Ouellette AJ, Slattery DK and Smitha LA. Photocatalytic inhibition of algae growth using TiO_2, WO_3, and cocatalyst modifications. Environmental Science & Technology, 2000,34(22):4754-4758.

[73]. http://norganix.com/

[74]. Qu ZZ. The bio-erosion resistance of concrete. Concrete, 1997, (4):34-36,39.

[75]. http://conseal.com/concrete-sealant-products/conblock-mic.html

[76]. Zhang B. Application and optimization of bactericide in concrete under sewage environment. Master Thesis, Shijiazhuang Tiedao University, China, 2018.

[77]. Hernandez M, Marchand EA, Roberts D, Peccia J. In situ assessment of active Thiobacillus species in corroding concrete sewers using fluorescent RNA probes. International Biodeterioration and Biodegradation, 2002,49(4):271-276.

[78]. Azam A, Ahmed AS, Oves M, Khan MS, Habib SS, Memic A. Antimicrobial activity of metal oxide nanoparticles against Gram-positive and Gram-negative bacteria: a comparative study. International Journal of Nanomedicine, 2012, 7:6003.

[79]. Chang YN, Zhang MY, Xia L, Zhang J, Xing GM. The toxic effects and mechanisms of CuO and ZnO nanoparticles. Materials, 2012,5(12):2850-2871.

[80]. Li J, Zhang YJ, Li YL, Song YB. Current state and development of quaternary ammonium salt bactericides. Detergent and Cosmetics, 2015,38(9):32-35,39.

[81]. McDonnell G and Russell AD. Antiseptics and disinfectants: activity, action, and resistance. Clinical microbiology reviews, 1999,12(1):147-179.

[82]. Shook WE. Twenty years of protecting concrete in sewers. Journal of Environmental Engineering, 1991.

[83]. https://www.conshield.com/

[84]. Kurihara Y, Takahashi J, Kamiike Y. Antibacterial agent for concrete, concrete

compositions and concrete products. Patent US 6752867 B1, 2004.

[85]. Kong LJ, Zhang B, Fang J, Wu LP, Wang CH. A type of antimicrobial corrosion concrete. Patent CN 106747062 A, 2016.

[86]. Cai ZY. Concrete material and preparation method for antibacterial and anticorrosive marine ecological engineering. Patent CN 106587855 A, 2017.

[87]. Han BG, Zhang LQ, and Ou JP. Smart and Multifunctional Concrete Toward Sustainable Infrastructures, Springer, 2017:299-311.

[88]. Janus M, Kusiak-Nejman E, Rokicka-Konieczna P, Markowska-Szczupak A, Zajac, K and Morawski AW. Bacterial inactivation on concrete plates loaded with modified TiO_2 photocatalysts under visible light irradiation. Molecules, 2019,24(17):3026.

[89]. Miyandehi BM, Feizbakhsh A, Yazdi MA, Liu QF, Yang J, Alipour P. Performance and properties of mortar mixed with nano-CuO and rice husk ash. Cement and Concrete Composites, 2016,74:225-235.

[90]. Hosseini P, Abolhasani M, Mirzaei F, Koohi M, Khaksari Y, Famili H. Influence of different types of nanosilica hydrosols on properties of sustainable white cement mortar. Journal of Materials in Civil Engineering, 2018,30(2).

[91]. Han BG, Ding SQ, Wang JL, Ou JP. Nano-Engineered Cementitious Composites: Principles and Practices. Springer, 2019.

[92]. Hosseini P, Hosseinpourpia R, Pajum A, Khodavirdi MM, Izadi H, Vaezi A. Effect of nano-particles and aminosilane interaction on the performances of cement-based composites: An experimental study. Construction and Building Materials, 2014,66:113-124.

[93]. Han BG, Ding SQ, Yu X. Intrinsic self-sensing concrete and structures: a review. Measurement. 2015; 59: 110-128.

[94]. Mao LX, Hu Z, Xia J, Feng GL, Azim I, Yang J, Liu QF. Multi-phase modelling of electrochemical rehabilitation for ASR and chloride affected concrete composites. Composite Structures, 2019,207:176-189.

[95] Han BG, Zhang LQ, Zeng SZ, Dong SF, Yu X, Yang RW, Ou JP. Nano-core effect in nano-engineered cementitious composites. Compos Part A: Appl Sci Manuf 2017; 95: 100-109.

[96]. Sangiorgio V, Uva G, Fatiguso F, Adam JM. A new index to evaluate exposure and potential damage to RC building structures in coastal areas. Engineering Failure Analysis, 2019,100:439-455.

[97]. Adam JM, Parisi F, Sagaseta, J, Lu XZ. Research and practice on progressive collapse and robustness of building structures in the 21st century. Engineering Structures, 2018, 173:122-149.

[98]. Adam JM, Buitrago M. Learning from failures in an emblematic building in Valencia, Spain. Engineering Failure Analysis, 2018,92:418-429.

[99]. Liu QF, Feng GL, Xia J, Yang J, Li LY. Ionic transport features in concrete composites containing various shaped aggregates: a numerical study. Composite Structures, 2018, 183:371-380.

[100]. Li L, Zheng Q, Li Z, Ashour A, Han B. Bacterial technology-enabled cementitious composites: a review. Composite Structures, 2019, 225, 111170,18p.