Cement & Concrete Composites 30 (2008) 839–847

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

# Cement-based biocide coatings for controlling algal growth in water distribution canals

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ARTICLE INFO

*Article history:*
Received 7 August 2007
Received in revised form 13 June 2008
Accepted 13 June 2008
Available online 4 July 2008

*Keywords:*
Biocide
Algae
Control
Concrete
Mortar

ABSTRACT

The germicidal effectiveness of various additives when blended within a microstructure of a cement based system was studied. The relationship between the chemical and physical characteristics of concrete surfaces and their ability to have an enhanced resistance to algal growth was documented through a novel set of laboratory and field testing. The main potential areas of application for these new cement composite systems involve the lining of canal surfaces where fixed-surface biocides are desirable to control biofouling. Different biocide formulations containing class F fly ash, silica fume, Zn oxide, copper slag, ammonium chloride, sodium bromide, and cetyl-methyl-ammonium bromide were evaluated for the mitigation of algal growth on concrete surfaces. Mortar coupons treated with these formulations were tested under laboratory and field conditions.

These new cement composite systems were compared with proprietary products that are commercially available and applied using a latex paint. Laboratory scale screening experiments showed that various concentrations of zinc oxide significantly inhibited algal growth even after nine months. It was observed that 20% zinc oxide in concrete produced optimal algal inhibition compared to other additives. Copper slag, ammonium chloride, sodium bromide, and fly ash, when added singly, also showed algal inhibition capabilities. Addition of zinc oxide and ammonium chloride (10% each) in mortar mix was as effective as expensive proprietary chemicals in reducing algal growth on concrete surfaces under laboratory and field conditions.



## 1. Introduction

Plain or reinforced concrete has been traditionally used for covering the surfaces of many canals, pipes, irrigation channels, and water treatment structures. The surfaces of concrete provide an ideal corrosion resistant, physically and chemically stable environment for exposure to potable or waste water. There is however a lack of understanding in the correlation between the nature and composition of the concrete with its biological characteristics in terms of a medium for water transportation and delivery. The purpose of this paper is to investigate if changes in the chemical composition of paste can result in suppression of algae growth on concrete surfaces in canals.

Prolonged exposure of any solid surface to water results in a series of physical, chemical, and biological events at the surface that form a community of microorganisms referred to as biofilm. The process starts with initial settlement of planktonic (free floating) microorganisms on the surfaces followed by the accumulation of an organic material layer (generally the extra-cellular polymeric substances (EPS) excreted by the attached microorganisms). The biofilm formation is influenced by types of microorganisms (biotic) and nature of surfaces and environmental conditions (abiotic) factors (Fig. 1).

Algae are among the most abundant and prolific microorganisms found in water bodies in the regions with sufficient sunlight and nutrients (nitrates and phosphorous). Growth of algae is quite common in irrigation canals that transport water to utilities [1]. This makes it difficult for the water utilities to provide drinking water that is not affected by algae and their byproducts. In addition to reduced flow rate in channels, algal growth results in the release of undesirable taste and odor compounds into the water during the summer months. In addition to taste and odor compounds, periphytic algae (that live attached to surfaces) have been implicated in releasing bio-toxins in water [2–9].

Problems associated with algal growth have stimulated drinking water treatment utilities to seek measures to decrease the algal growth in open lined concrete canals and water storage structures. Historically, chemical based antifouling (biofilm inhibition and disruption) strategies such as copper application have been used both

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0958-9465/$ - see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.cemconcomp.2008.06.012

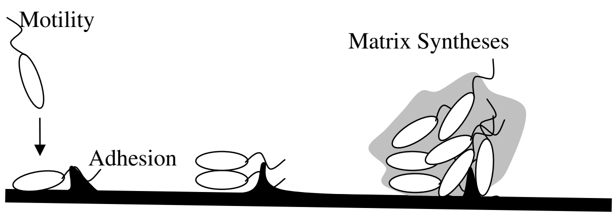



**Fig. 1.** Events in the biofilms formation.

in fresh water and marine environments. Organic polymers were introduced as algaecide as early as middle part of 20th century. By 1970s tributyltin (TBT) became the major antifouling agent in the marine industry. Globally, TBT antifouling coatings were estimated to save ship owners over two billion dollars annually in fuel costs. In the United States the cost benefits from the use of TBT coating was estimated to be from 100–130 million dollars annually. However, the toxic impact of TBT on non-target organisms, such as fish became evident by early 1980s, and its use in the United States was banned in 1988 and will be completely phase out by 2008 [10,11].

Currently, more that 18 chemicals are used as antifouling agents throughout the world [12–13]. Out of those, nine chemicals are approved for use by Health and Safety Executive (HSE) in the UK [14–15]. As a result of extensive use of these alternative chemicals, many coastal areas with boating activities have been polluted [16]. Antifouling paints such as EP2000 and Sun Wave have been recently introduced; however, they may be too expensive and may not be cost effective for low-end applications in fresh water environments [17]. Since alternatives to TBT are expensive and toxic, there is an eminent need for safer, effective, and less toxic antifouling agents, especially for large surface areas of concrete canals.

For fresh water applications, the alternate antifouling strategies must be cost effective and compatible with concrete base. One way to quantify algae content is through the measurement of chlorophyll content and its three types referred to as chlorophyll-*a*, -*b*, and -*c*. Heavy metal accumulation in algae has been known to cause chlorophyll (green pigment) reduction in algal cell. High concentrations of heavy metals such as Zinc can cause thinning and elongation of algae cells with a reduction in chlorophyll-*a*, and chlorophyll-*b* content up to 48% in just one week [18–20]. Exposure to such conditions disrupts algal growth or even causes death of an algae cell within a few days, however, environmental condition can

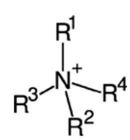



**Fig. 2.** General structure of quaternary ammonium compounds (R = any of the alkyl groups and any of which may be connected).

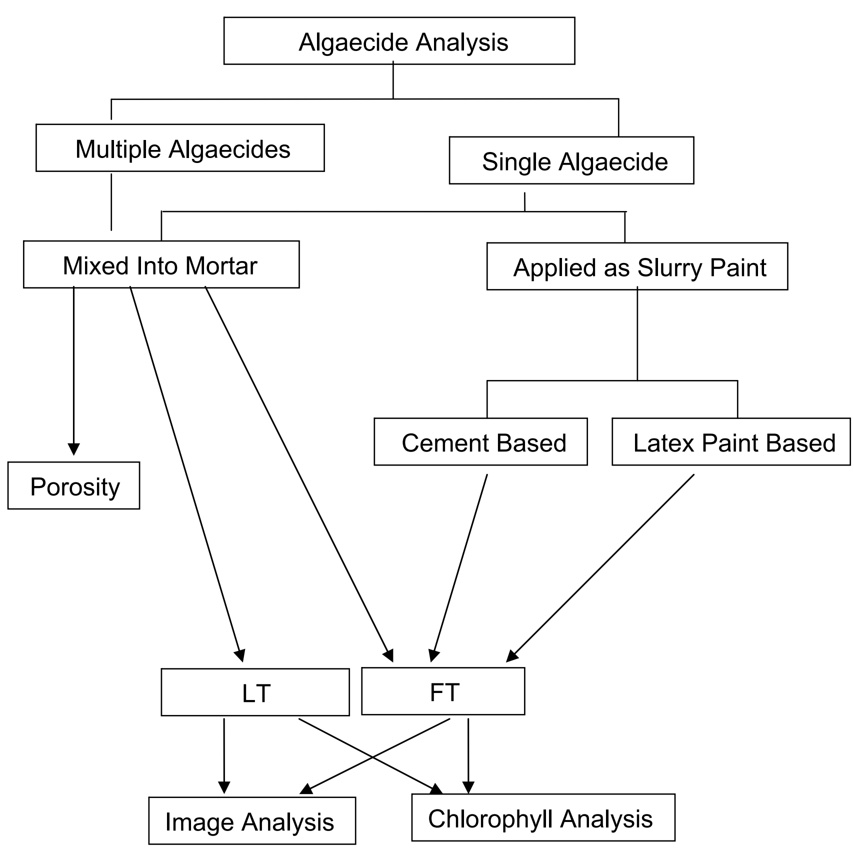



**Fig. 3.** Schematic description of scope of the study (LT: laboratory scale testing; FT: field scale testing; the image analyses and porosity data has been submitted for publication in the ASCE Journal of Environmental Engineering).

**Table 1**
Selection criteria for biocides and additives

| Material | Selection criteria |
|---|---|
| Zinc oxide | Used as biostatic/biocidal material in other areas but has not been tried as an admixture in concrete. Seems suitable for water carrying structures because of low water solubility |
| Fly ash | Used as a mineral admixture and results in densification of the paste aggregate interface zone and general reduction in capillary porosity |
| Copper slag | Copper has been reported to have biostatic effect. With a high Iron Oxide content, Copper slag has been used as an admixture to increase the strength and durability of concrete |
| Ammonium chloride | Biocide generally used in low-cost marine environment |
| Sodium bromide | Biocide anciently used for painting ships and marine |
| Cetyl-trimethyl-ammonium bromide | New compound on the market, expected to have broader biocidal activity |

modify the lethal effect of heavy metal on algal species [21–23]. The US EPA considers Zinc ions to be toxic to aquatic life because they hinder the natural food chain cycle of the aquatic environment in pH ranges of 5–7. According to National Academy of Sciences, Zinc is also an essential nutrient for aquatic and terrestrial organisms, and it is needed in low levels for the synthesis of nucleic acid and enzymes [24].

Quaternary ammonium chloride compounds (Quats) represent another option for antifouling applications (Fig. 2). Quats are normally a variation of Benzalkonium chloride, and have been used as antimicrobial agents for long time; only recently they have been used as algaecides [25]. The germicidal effectiveness of these materials when blended within the microstructure of a cement based system has not been evaluated yet.

Antifouling chemical agent can be applied by using different strategies. In general, biocides fixed on the surfaces are more effective in aquatic environments. The currently available fixable biocides when applied as paints are not cost effective for freshwater environments. We hypothesize that Quats and heavy metal based algaecide chemicals when added into mortar mix or latex based paint can provide long lasting (residual) algaecidal effect and will provide a cost effective antifouling strategy for fresh water environments. The focus of this study was to investigate various chemicals as fixed biocides to control or mitigate algal growth on solid surfaces of concrete materials used for canal lining. The study was used to rank several potential additives and identify biocide chemicals that can be used as single or combined additives in mortar mix or in latex paint for coating the sides of water storage and carrier structures. The research methodology was based on changing the chemical and physical characteristics of surfaces to improve/enhance their resistance to algal growth. The mitigation effect was quantified by algal biomass growth on mortar surfaces containing different biocide formulations.

## 2. Materials and methods

### 2.1. Experimental plan

An exploratory effort was conducted to identify promising cost effective biocides (from a list of 50 formulations) in freshwater aquatic applications. According to Fig. 3, two strategies were used to apply fixed biocides to a mortar coupon. The first approach was to blend the biocides in mortar during the mixing process while the second approach introduced biocides into a latex based paint that was applied to the surface of mortar coupons. The steps involved in the data collection and sample preparation of the testing program are shown in the Fig. 3. Two types of studies were conducted using algaecides used in mortar and in a surface coat. The methods of measurement consisted of both image analysis and also chlorophyll extraction. This paper only addresses the results of chlorophyll extraction method and compares the laboratory conducted tests with the field sample specimens.

### 2.2. Selection of materials and mortar coupon preparation

Type I/II Portland cement (PC) was used for all mortar mix formulations. Silica sand (SS) was used as a filler material. The selection criteria for the biocides and additives are presented in Table 1.

**Table 2**
Mortar mix design schedule

| Treatment | Water/cement | Sand/cement | Chemical admixture (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | ZnO (%) | Copper slag (%) | Ammonium chloride (%) | Sodium bromide (%) | Cetyl-metyl-ammonium chloride (%) | Fly ash | Comments |
| A | 0.45 | 0.5 | 10 | | | | | | |
| B | 0.45 | 0.5 | 20 | | | | | | |
| C | 0.45 | 0.5 | 25 | | | | | | |
| D | 0.5 | 0.5 | 30 | | | | | | |
| E | 0.45 | 0.7 | | 20 | | | | | |
| F | 0.45 | 0.3 | | | 10 | | | | |
| G | 0.4 | 0.3 | | | 20 | | | | Failed |
| H | 0.45 | 0.3 | | | | 10 | | | |
| I | 0.45 | 0.3 | | | | 20 | | | |
| J | 0.4 | 0.3 | | | | | 10 | | |
| K | 0.45 | 0.3 | | | | | 10 | | Failed |
| L | 0.45 | 0.5 | 10 | | | | | 10 | |
| M | 0.5 | 0.5 | 20 | | | | | 10 | |
| N | 0.5 | 0.5 | 25 | | | | | 10 | |
| O | 0.45 | 0.3 | 10 | | 10 | | | | |
| P | 0.45 | 0.3 | 10 | | | 10 | | | |
| Q | 0.45 | 0.3 | 10 | 10 | | | | | |
| R | 0.45 | 0.3 | 20 | 10 | | | | | |
| S | 0.45 | 0.3 | 10 | 20 | | | | | |
| T | 0.5 | 0.3 | 20 | 20 | | | | | |
| U | 0.5 | 0.3 | 10 | | 5 | | | 5 | |
| V | 0.5 | 0.3 | | | | | | | |
| W | 0.5 | 0.3 | 10 | 5 | 5 | | | | |
| X | 0.5 | 0.3 | | | | | | | |

The sand/cementitious solids ratio of 0.8 and water/cementitious solids ratios of 0.5 were used for all specimens as presented in Tables 2 and 3. Mortar samples were prepared according to the mix design details as shown in Table 2 using Portland cement with various concentrations (10–30%) of zinc oxide (ZO), sodium bromide (SB), ammonium chloride (AC), copper slag (CS), and

**Table 3**
Mortar mix and paint composition

| Treatment | Water/cement ratio | Sand/cement ratio | Chemical composition and quantity of paint additive in g/l | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | ZnO | Copper slag | Ammonium chloride | Sodium bromide | Cetyl-methyl-ammonium chloride | proprietary products and controls |
| AA | 0.4 | 0.8 | 16.67 | | | | | |
| AB | 0.4 | 0.8 | 33.33 | | | | | |
| AC | 0.4 | 0.8 | 83.33 | | | | | |
| AD | 0.4 | 0.8 | 166.67 | | | | | |
| AE | 0.4 | 0.8 | | 16.67 | | | | |
| AF | 0.4 | 0.8 | | 33.33 | | | | |
| AG | 0.4 | 0.8 | | 83.33 | | | | |
| AH | 0.4 | 0.8 | | 166.67 | | | | |
| AI | 0.4 | 0.8 | | | 16.67 | | | |
| AJ | 0.4 | 0.8 | | | 33.33 | | | |
| AK | 0.4 | 0.8 | | | 83.33 | | | |
| AL | 0.4 | 0.8 | | | 166.67 | | | |
| AM | 0.4 | 0.8 | | | | 16.67 | | |
| AN | 0.4 | 0.8 | | | | 33.33 | | |
| AO | 0.4 | 0.8 | | | | 83.33 | | |
| AP | 0.4 | 0.8 | | | | 166.67 | | |
| AQ | 0.4 | 0.8 | | | | | 16.67 | |
| AR | 0.4 | 0.8 | | | | | 33.33 | |
| AS | 0.4 | 0.8 | | | | | 83.33 | |
| AT | 0.4 | 0.8 | | | | | 166.67 | |
| SW | 0.4 | 0.8 | | | | | | Sun Wave |
| EP | 0.4 | 0.8 | | | | | | EP 2000 Ardex® |
| CTRL1 | 0.4 | 0.8 | | | | | | Mortar control |
| CTRL2 | 0.4 | 0.8 | | | | | | Paint control |

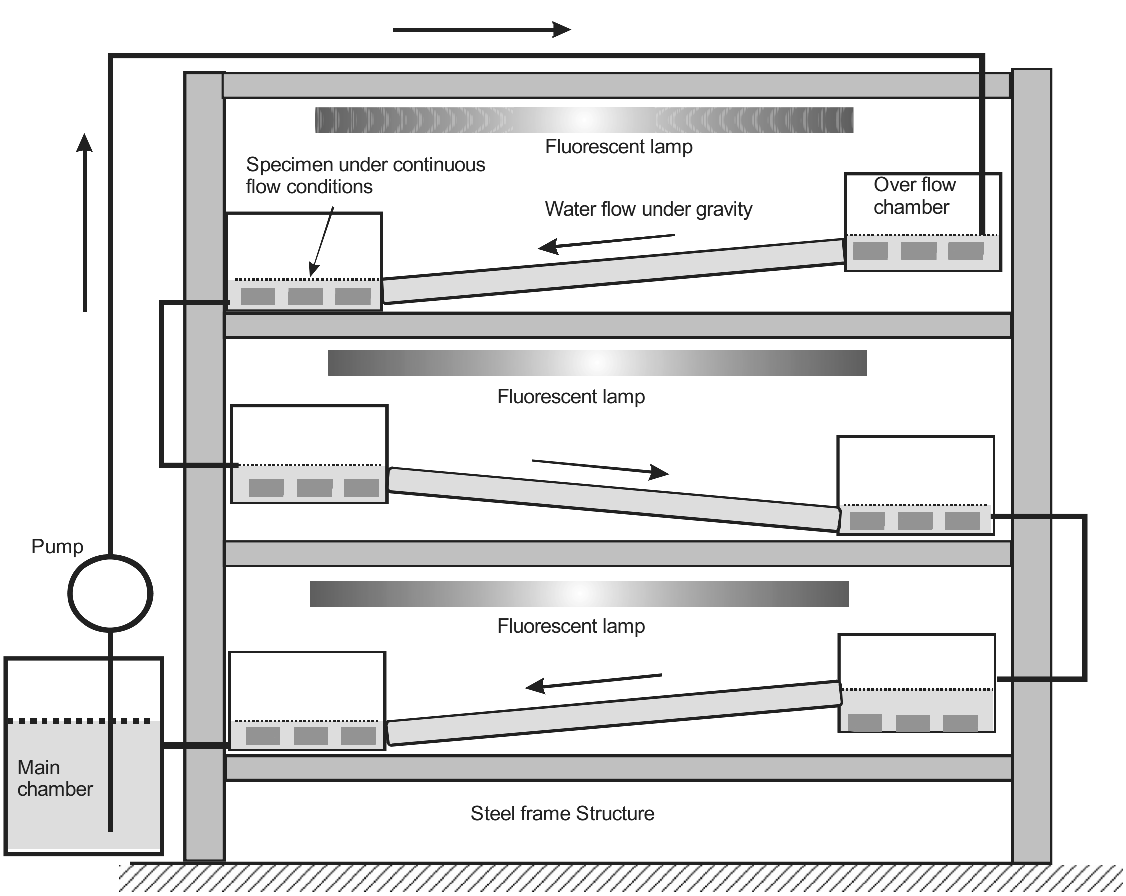



**Fig. 4.** Schematic diagram of algae growth reactor with coupons under incubation.

**Table 4**
The components of the BG11 medium for algal growth

| Stock solution | Components |
|---|---|
| Trace minerals – add to 1 l of distilled water | 2.86 g – $H_3BO_3$<br>1.81 g – $MnCl_2 \cdot 4H_2O$<br>0.22 g – $ZnSO_4 \cdot 7H_2O$<br>0.39 g – $Na_2MoO_4 \cdot 2H_20$<br>0.079 g – $CuSO_4 \cdot 5H_2O$<br>0.049 g – Co $(NO_3)_2 \cdot 6H_2O$ |
| BG11 without Fe, phosphate and carbonate – add to 900 ml of distilled water | 149.6 g – $NaN0_3$<br>7.5 g – $MgS0_4 \cdot 7H_2O$<br>3.6 g – $CaCl_2 \cdot 2H_2O$<br>0.60 g – citric acid<br>1.12 ml – NaEDTA, pH 8.0, 0.25 M<br>100 ml – trace minerals |
| Other components | Ferric ammonium citrate – 600 mg per 100 ml of $H_2O$<br>$Na_2CO_3$ – 2 g per 100 ml of $H_2O$<br>$K_2HPO_{4\_}$ – 3.05 g per 100 ml of $H_2O$ |
| To make 1 l of BG 11 solution, add these components with distilled water and autoclave for 230 min | 100 ml – BG11 without Fe, phosphate and carbonate<br>10 ml of ferric ammonium citrate<br>10 ml of $Na_2CO_3$<br>10 ml of $K_2HPO_4$ |

cetyl-methyl-ammonium bromide (CAB). The standard mixing method according to ASTM (C 305–99, C 685–00a) was used [26]. Control mortar coupons 25 mm × 25 mm × 275 mm in dimension were prepared using Portland cement (PC, type I/II) meeting ASTM designation C-150 in addition to additives. The samples were cured for 14 days in saturated calcium hydroxide solution. After this period the bars were sliced to 25 × 25 × 12 mm sized coupons using a water-cooled diamond blade circular saw. Individual coupons were placed in the algae growth reactor described in the next section.

### 2.3. Algae growth reactor

A three tier steel frame of 244 cm (height) × 214 cm (length) × 92 cm (depth) was manufactured with each tier having a height of 61 cm (Fig. 4). Within each layer, three open water channels were placed at a slope of 3%. The channels were constructed of PVC pipes cut in half lengthwise. These water channels were connected to plastic containers 61 cm × 61 cm in dimension. These plastic containers were used to stabilize the flow and transfer the water from one tier to the next.

A 284 l (75 gallon) plastic tank was used as the main water reservoir while a 72 l (19 gallon) plastic tank was used at the top of the frame to serve as the overflow tank. A magnetic driven pump (Little Giant, OK) was used to lift water from the main tank to the overflow tank via a 2 cm (0.75 in.) PVC pipe. Thereafter, water flowed down the open water channels under gravity. To provide the illumination necessary for the growth of algae, four sets of 60 W fluorescent lamps were installed above the water channels on each tier. The lights were left continuously on. The city of Tempe, AZ, tap water was used to recharge the reactor due to evaporation losses. The study was conducted at ambient room temperature of 25 ± 2 °C. The entire duration of study lasted six months.

#### 2.3.1. Growth of algae in reactor

The growth reactor was seeded with a mixture of algae collected from local water bodies (CAP and SRP canals). Initially, nutrients medium BG 11 (Table 4) was added to the reactor to help initiate algal growth [27]. After the reactor was fully colonized with algae, mortar coupons made with different biocide treatments as discussed above were submerged in the channels.

### 2.4. Screening under field conditions

Field evaluation samples were fixed on a plastic tray sheet and submerged in Arizona canal down stream of Granite Reef Dam. Fig. 5 shows the placement of the mortar coupon trays inside the canal along the sloped edge of the water channel. The specimens were periodically removed from the canal and analyzed for algal biofilm. Fig. 6 shows the succession of algal biofilm growth on samples during the two months of incubation in Arizona canal (field conditions). It is noted that significant amount of algae formed on these controlled surfaces.

**Fig. 5.** Placement of samples in the Arizona canal.

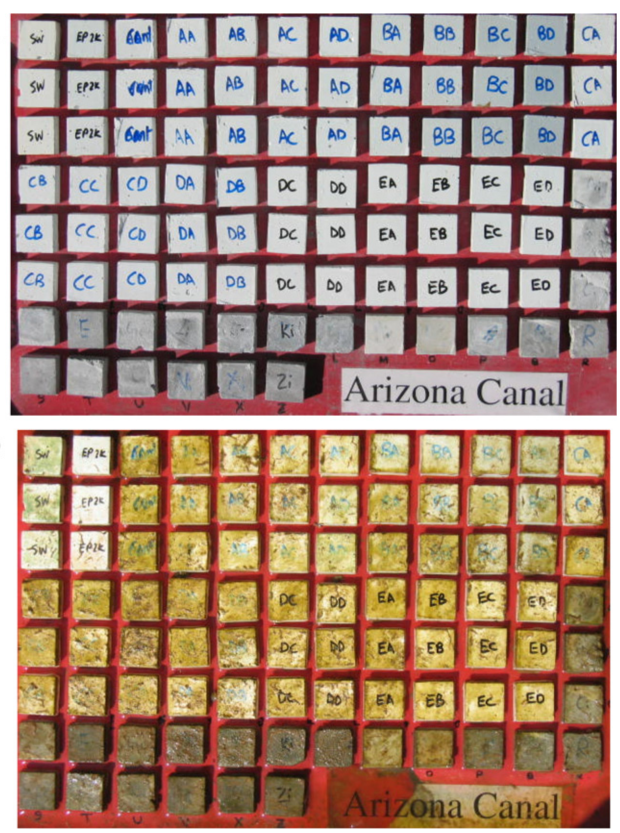
a
b



**Fig. 6.** Succession of algal biofilm growth on samples incubated in Arizona canal: (a) specimens prior to placement and (b) specimen indicating algae growth after two months of field exposure.

### 2.5. Sample collection procedure

The samples were taken out of the reactor by lifting them sideways to ensure that only the attached or periphytic algae remained on the sample and to avoid any bias due to the planktonic algae. Once the sample coupons were taken out, the algal biomass was harvested using plastic spatulas. During the scraping process, the coupon surfaces were rinsed with distilled water to ensure that all the algal biomass was captured into the beaker.

### 2.6. Algal biomass quantification

The chlorophyll extraction method is commonly used for quantification of algal biofilm. The chlorophyll analysis was conducted based on the Standard Methods (19th Edition, 1995, No. 10200 H. Chlorophyll) [28]. The procedure involves the disruption of algal biofilm and extraction of chlorophyll contents for different ultraviolet light absorbance analyses. The acetone extracts of chlorophylls were transferred to cuvettes and analyzed for different types of chlorophyll using a HACH DR 4000U spectrophotometer. For this study the spectrophotometer was programmed to take successive readings at four wavelengths (750, 664, 647 and 630 nm) for turbidity, chlorophyll-*a*, chlorophyll-*b*, and chlorophyll-*c*, respectively (only total chlorophyll data is presented here).

The chlorophyll contents were calculated using standard methods # 10200H (Standard Methods 19th Edition). The various wavelengths measured were substituted into the equations provided in the standard methods and the concentrations of chlorophyll-*a*, -*b*, and -*c*, were calculated. For each concentration, the optical density (OD) reading for turbidity was subtracted from the respective OD reading for that particular chlorophyll type. Once the turbidity corrected concentrations of the extract solutions were calculated, the algal biomass of that substrate was determined as mg chlorophyll/$m^2$ of substrate surface.

## 3. Research approach

The first group of biocides investigated for use in concrete materials included inorganic compounds of copper and zinc metal (zinc oxide and copper slag). These compounds were either mixed in or applied on the surface of mortar coupons to mitigate algal growth on these surfaces. The highest concentrations of these compound used was 10% (w/w), which though seem high when compared with the average flux rates (rate of emissions from antifouling paint) of dissolved copper of 3.7–4.3 μg/$cm^2$/day reported by other workers [29]. The typical copper ion release rates from pleasure crafts and naval ships are 8.2 μg/$cm^2$/day and 3.8 μg/$cm^2$/day [30]. The composition of copper slag primarily contains iron oxides and only trace amounts of copper are present. It is important to point out that copper emission from mortar coupons was very slow and concentration of copper ion in test water in algal growth chamber was always below the US EPA's chronic water quality criterion of 3.0 μg/l. This might be due to the fact the microbial biofilm growth on the surface act as a barrier and result in controlled release of the heavy metal ions from test [30]. Since the objective of these heavy metal additive is to inhibit algal growth on surfaces, upon release from the concrete coupons the heavy metal ions first get in contact with the algal cells attached to the coupons surface, therefore maximizing the effectiveness of these ions.

Zinc oxide is another inorganic compound investigated as a concrete admixture. Zinc is one of the environmentally important metals that is not biodegradable and travels through the food chain via bioaccumulation [31]. Therefore there is significant interest regarding its environmental fate [32], and its toxicity for humans at levels of 100–500 mg $day^{-1}$ [33]. World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg $l^{-1}$ [34]. The concentration of zinc ions in test water in the algal growth reactor were always below the WHO drinking water standards (data not shown). The mode of action of heavy metals on algae is generally not known. High concentrations of zinc and lead accumulate in the vacuoles (air filled bubbles inside a microbial cell) of algae cells and are toxic to these organisms [17]. High zinc concentrations have been reported to cause thinning and elongation of algae cells with a reduction in chlorophyll-*a*, and chlorophyll-*b* content up to 48% after one week exposure [17]. However, in the present study growth mitigation effect was visible even after several months. The slow release of ion due to biofilm layer on coupon surfaces may be responsible for their prolonged effectiveness. Moreover, chlorophyll reduction and breakdown of photosynthesis in algae exposed to heavy metal stressors have been reported. Such conditions have resulted in inhabitation of algal growth or even death of an algae cell within a few days [18]. The US EPA considers zinc ions to be toxic to aquatic life because they hinder the natural food chain cycle of the aquatic environment between pH values of 5 and 7. According to National Academy of Sciences, zinc is also an essential nutrient for aquatic and terrestrial organisms, and it is needed in low levels for the synthesis of nucleic acid and enzymes [21]. Solubility of zinc oxide depends on temperature and pH and ranges from 2.92 mg/l at 18 °C to 15.5 mg/l at 29 °C; it is stable as a solid above 39 °C. The solubility of zinc oxide decreases at high pH with a minimum value of 9.3 [21]. In the environment it does not go through major microbial transformation. These properties of zinc oxide make it an optimal additive for the concrete lining of canals in central Arizona. In Arizona water pH is mostly above 7 and summer temperatures are mostly above 39 °C. These conditions favor the stability of zinc oxide and minimize its water solubility. Since high summer temperatures are conducive to mass algae production, the stabilization of zinc oxide at such temperatures makes it perfect choice as a fixed biocide for aquatic environments in the southwestern United States.

## 4. Experimental results

### 4.1. Inhibitory compounds mixed into mortar

#### 4.1.1. Single compounds

Single biocides were mixed in mortar and their effect on algal growth on coupons under laboratory and field conditions were studied. Results are presented in Fig. 7. Under laboratory conditions, control mortar coupons without any additives collected as much as 96.8 mg/$m^2$ of total chlorophyll. The additives were used in different substitution levels, for example mortar coupons with 10%, 20%, 25%, and 30% zinc oxide resulted in 90, 68, 130, and 114 mg/$m^2$. Similarly, optimum levels were determined in each single phase coupons with 20% copper slag, 10% ammonium chloride, 10% sodium bromide, and 20% sodium bromide yielding 113, 93, 85, and 61 mg/$m^2$ of total chlorophyll, respectively. Test results indicate that among all the samples tested, 20% zinc oxide and 20% and sodium bromide were the optimum level that yielded 68 mg/$m^2$ and 60 mg/$m^2$ of total chlorophyll producing the most effective algal inhibition compared to the control coupon (Fig. 7).

The laboratory test data were compared to field conditions that are reported Fig. 7. Under field conditions the mortar coupons with 20%, zinc oxide yielded 148 mg/$m^2$ of total chlorophyll which is as much as twice the laboratory values. Under field conditions the coupons with 10% ammonium chloride, 10% sodium bromide, and 10% cetyl-methyl-ammonium bromide yielded 96, 59, 49, and 52 mg/$m^2$ of total chlorophyll, respectively. The data

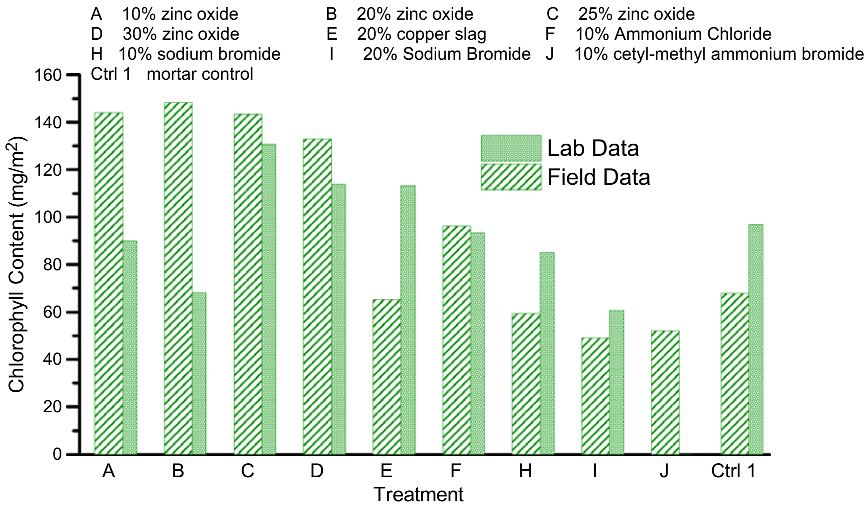



**Fig. 7.** Algal growth (chlorophyll contents) on mortar coupons containing different concentrations of zinc oxide, copper slag, ammonium chloride, or sodium bromide under laboratory and field conditions.

presented in Fig. 7 shows that sodium bromide at 20% and cetyl-trimethyl-ammonium bromide at 10% concentrations are most effective for inhibiting algal growth on mortar coupons.

*4.1.2. Binary and tertiary compounds*

Multiple biocides were mixed in mortar coupons to evaluate their collective impact on algal growth under laboratory and field conditions and results are presented in Fig. 8. The complementary effects of fly ash, ammonium chloride, sodium bromide, and copper slag in various combinations with zinc oxide mixed in mortar are shown in Fig. 8. In the binary system of zinc oxide–flyash systems, mortar coupons with 20% zinc oxide plus 10% fly ash (20–10) yielded optimum levels of 99 $mg/m^2$ of total chlorophyll. Where as at the 10% Zinc oxide levels, coupons with 10–10 (%) zinc oxide and ammonium chloride and sodium bromide yielded 62 and 118 $mg/m^2$ of total chlorophyll respectively. Supplementation of zinc oxide with copper slag (in varying concentrations) yielded variable total chlorophyll concentrations in the range of 103–120 $mg/m^2$ of total chlorophyll. Similarly, mortar coupons containing three biocides were also analyzed for algal biofilm growth. Mortar coupons with 10–5–5 (%) zinc oxide-fly ash-ammonium chloride or sodium bromide yielded about 106 and 104 $mg/m^2$ of total chlorophyll. At the 10–5–5 (%) zinc oxide–copper slag–ammonium chloride or sodium bromide levels results in the range of in 95 and 86 $mg/m^2$ of total chlorophyll, respectively. Therefore, the most effective algal inhibition was achieved on mortar coupons containing 10% zinc oxide and 10% ammonium chloride.

Mortar coupons with multiple biocides were evaluated under field conditions and the results are presented in Fig. 8. The mortar coupons containing variable zinc oxide and 10% flyash yielded 20–10 ratio as the optimum level with 96 $mg/m^2$ of total chlorophyll. The mortar coupons containing 10–10 (%) zinc oxide–ammonium chloride or sodium bromide yielded 71 and 65 $mg/m^2$ of total chlorophyll, respectively. Similar results were obtained when zinc oxide was complemented with varying concentrations of copper slag. Copper slag contains mostly iron oxides of fayalite ($Fe^{+2}2SiO_4$) and magnetite ($Fe_3O_4$) [35]. Total chlorophyll concentrations of 56 $mg/m^2$ were obtained as the optimum level with the 20–10 (%) zinc oxide–copper slag, respectively. Similarly, mortar coupons with three biocides were also analyzed for algal biofilm or chlorophyll contents. Among the various combinations tested coupons containing 10–5–5 (%) zinc oxide–ammonium chloride–copper

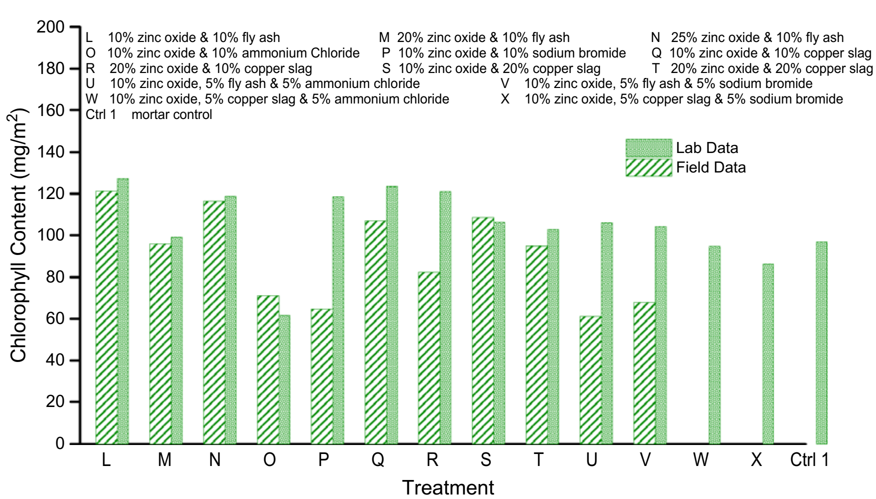



**Fig. 8.** Algal growth (chlorophyll contents) on coupons containing different concentrations of zinc oxide in combination with copper slag, ammonium chloride, and/or sodium bromide under laboratory conditions.

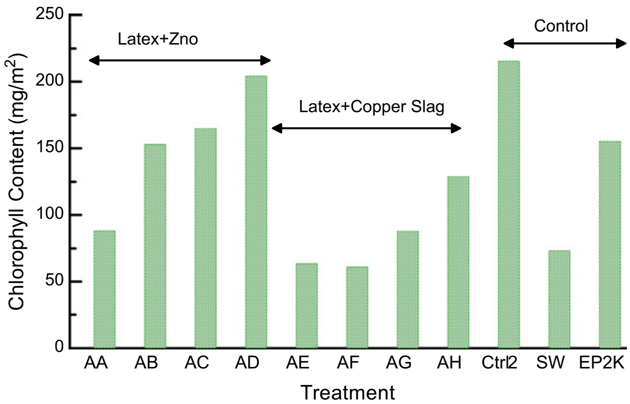



**Fig. 9.** Algal growth on mortar coupons coated with latex paint containing different concentrations of zinc oxide and copper slag (under laboratory conditions).

slag with 61 mg/m$^2$ of total chlorophyll responded most positively. The mortar coupons containing tertiary compounds with Sodium bromide were not tested under field conditions as the surfaces were too weak and uneven to be attached to the substrate.

Many of the synergistic observations require further evaluation. For example, effectiveness of single and binary/tertiary compounds in reducing biofilm growth needs to be further addressed. The complementary effects of fly ash, ammonium chloride, sodium bromide, and copper slag in combination with zinc oxide are not fully understood and it is not clear why such combinations appear to be beneficial.

### 4.2. Inhibitory compounds applied as paint

Previous studies have indicated that quaternary amine-containing organosilicon salts (referred to as Quats) immobilized on a variety of substrates, exhibited algicidal activity against wide range of algal species [36]. Quaternary ammonium compounds at a concentration of 0.16–0.5 fl. oz per gallon of water provide effective control of algal growth under green house conditions [24,37,38].

Effects of latex paint-based biocide coatings on algal growth on mortar coupons were investigated under laboratory conditions. Latex paints with different concentrations of zinc oxide, copper slag, ammonium chloride, sodium bromide, and cetyl-methyl-ammonium bromide (Table 3) were applied on mortar coupons and the results are shown in Figs. 9 and 10. The mortar coupons coated with latex paint contained various proportions of three different constituents. Use of 16.67 g/l of zinc oxide or ammonium chloride yielded 88 and 60 mg/m$^2$ of total chlorophyll as shown in Fig. 9, respectively. Copper slag and sodium bromide used at 33.3 g/l yielded 61 and 51 mg/m$^2$ of total chlorophyll, respectively (Figs. 9 and 10), while the best performance by Cetyl-methyl-ammonium was at 121 mg/m$^2$ (Fig. 10). These results are comparable with major algaecide paints on the market, Sun Wave (SW) and EP 2000, which yielded 74 and 155 mg/m$^2$ of total chlorophyll, respectively. The results show that latex paint with 16.67 g/l of zinc oxide provides algal inhibition comparable or superior to the commercially available products. Furthermore use of small dosages of copper slag in standard paint is as effective as some of the commercial products used.

In the present study 10% (w/w) quaternary ammonium did not provide significant control of algal growth on treated surfaces. As is it known that the structural variants of quaternary ammonium show different level of germicidal activities. Based on the results of this study it can be concluded that cetyl-methyl-ammonium bromide is not an effective algaecidal agent. Quaternary ammonium compounds are available as bromide, chloride and methylsulphonate salts. The quaternary ammonium compounds containing dibromide, dichloride and chloride formulations have been reported to be the most potent herbicides and germicides [39]. The quaternary ammonium compound used in the present study was a mono-bromide compound. Although better algaecide effect can be achieved by the application of dibromide, dichloride, and chloride formulations, the adverse health effects of these formulations to humans are well documented [40]. Diquat (dibromide) produces lung damage although it is not concentrated selectively as paraquat (dichloride). However, diquat has severe toxic effects on the central nervous system that are not typical of paraquat poisoning. Therefore application of these formulations to control algal growth in water bodies used as drinking water source might not be a good strategy.

Different formulation performed differently under field and laboratory conditions. The disparity in laboratory and field can be ascribed to variation in type of algae present in both systems. The algal complex in the laboratory scale algal reactor was less

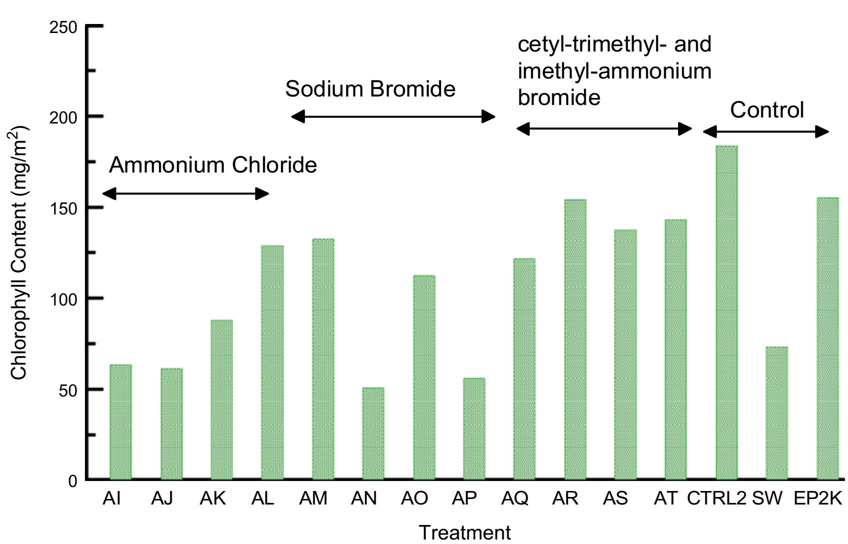



**Fig. 10.** Algal growth on mortar coupons coated with latex paint containing different concentrations of ammonium chloride, sodium bromide and cetyl-trimethyl-ammonium bromide (under laboratory conditions).

diverse than the field, which might be a reason for difference in the performance of these formulations. Additionally, under field conditions high flow and soil erosion resulted in the accumulation of a fine layer of clay on sample coupons. This layer might have resulted in change in the response of different formulations.

## 5. Conclusions

This study identifies the chemicals that can be introduced in concrete mixtures in order to enhance algaecide properties of concrete surfaces. The study provided quantitative results regarding the algal control without imparting an adverse toxic response in the subjects/environment. Based on the results of the present study it can be concluded that addition of "off-the–shelf" chemicals such as zinc oxide and ammonium bromide in a mortar mix can be as effective as or even better than many expensive proprietary chemicals in reducing algal growth on concrete walls of water storage and conveyance structures.

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