Influence of Concrete Properties on the Initial Biological Colonisation of Marine Artificial Structures

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Abstract:

Artificial marine infrastructures now cover large stretches of the available natural shoreline in many parts of the world. This is having a substantial impact on the local marine ecosystems as biodiverse natural hard substrata are being replaced with man-made structures, which have been shown to support lower levels of biodiversity.

The ecological value of artificial coastal structures could be enhanced through careful design of pre-fabricated ecologically engineered units. Material selection is a critical parameter in the design of these units. To maximise the potential of concrete units to support and increase biodiversity, this paper explores the

impact of binder composition, aggregate type and plasticiser on surface chemistry and early biofilm formation which influence subsequent colonisation. Experiments in the current study have shown that the addition of ground granulated blast-furnace slag (GGBS) to the mix can increase the levels of biodiversity supported while maintaining engineering performance requirements in terms of strength, chloride resistance and alkalinity. Conversely the aggregate type and use of a plasticiser have a minor influence. In particular, the addition of GGBS was shown to increase the biomass of diatoms, cyanobacteria and green algae and barnacle abundance one month after immersion on both sheltered surfaces and those exposed to wave action. Results suggest that concrete composition can alter the surface chemistry of artificial structures and thereby can improve the ecological value of these structures as habitats for marine life.

Key words: Artificial Marine Structures, Concrete Design, Ecological Engineering, Biodiversity Enhancement, Biofilm, Early colonisation.

1. Introduction

More than 70% of countries with shorelines have their largest cities built on the coast [1]. Almost half of the world's population is now estimated to live in coastal areas and that figure is predicted to double by 2025 [2]. As the coastal population

has increased, more pressure has been put on coastal ecosystems through habitat conversion, increased pollution and greater demand for marine resources [1]. The change from natural to artificial coastal habitats is considered one of the main threats to coastal ecosystem integrity and sustainability [3]. These marine developments are generally associated with fragmentation and loss of natural habitats, damaged seascapes and reduced biodiversity [1]. Despite the rapid development of artificial marine structures across the world, our understanding of the colonisation of these environments by epibiotic plants and animals is limited [4].

Natural habitats such as rocky reefs provide habitats for a large number of intertidal and subtidal species of plants and animals [5], and are being replaced by artificial structures. These marine infrastructures can provide significant habitat for epibiota and also attract mobile subtidal species during high water and birds during low water [6, 7]. However, the epibiotic assemblages they support are often depauperate compared to natural habitats [5, 8, 9, 10]. Natural habitats provide shade, moisture and refuge from predation and disturbance through their rough surfaces, pits, crevices and rockpools [11]. In contrast, artificial structures typically fail to provide these textures and microhabitats, with a notable impact on the organisms that would otherwise colonise these surfaces [12].

Marine biofilms form rapidly on coastal structures and consist of dynamic communities of diatoms, cyanobacteria and green algae which form within a matrix of extracellular polymeric substances [13, 14]. These biofilms act as one of the main food sources for grazing invertebrates [15, 16]. In addition, biofilms are known to emit chemicals used as cues for settlement by the larvae of fouling organisms [17, 18]. They are also an important contributor to ecosystem functioning and productivity [19]. Factors such as microtopographic complexity and substrate surface chemistry have been reported to influence the development and composition of biofilm communities [20, 21]. As the physiochemical properties of concrete may vary widely, biofilm composition may also be altered. The influence of variation in concrete properties may also vary depending on the environmental context, for example in relation to exposure to wave action. Understanding the direct effect that concrete composition will have on biofilm community structure is not only important due to their role as a food source for grazing invertebrate species, but also to understand the indirect effect that changes in biofilm community structure may have on the colonisation of invertebrate and macroalgal species as succession progresses.

It is proposed that the ecological value (i.e. local biodiversity and local biomass) of artificial marine infrastructure could be increased through careful design of pre–fabricated ecologically engineered units [22, 23, 24, 25]. Material selection

is a crucial parameter in the design of these units. Reinforced concrete often plays an important role in the design process due to its ease of production, relatively low cost and its suitability for mass construction. Portland cement concrete is widely used [23], and has been found to offer good support for colonising organisms with calcareous skeletons (e.g. oysters, serpulid worms, barnacles and corals), as they deposit calcium carbonate onto the surface in a biogenic build-up process [26]. That said, the high surface alkalinity of the concrete (pH 12-13 compared to 8 of seawater) could reduce settlement of other less alkotolerant species marine organisms and result in communities dominated by a few alkotolerant taxa [27]. By adding pozzolanic industry by-products such as ground granulated blast-furnace slag (GGBS), fly-ash and silica fume to the concrete mix, it is possible to reduce the alkalinity of the concrete and potentially create a more suitable surface for colonisation by marine species [28].

Concrete possesses an inherent reserve of alkalinity, and this is sometimes expressed through its capacity for neutralizing acids by hydrolysis of the products of anodic dissolution. This inhibitive property of concrete arises from its ability to neutralise the acid produced by hydrolysis of the products of anodic dissolution. This inhibitive property can be characterised by its acid neutralisation capacity (ANC). The ANC is also considered a key parameter in characterising concrete corrosion resistance [29]. It is also a useful measure to

describe the concrete alkalinity. The cement content, binder type and free water to cement ratio play a significant role in ANC of concrete [30].

Furthermore, the addition of pozzolanic industry by-products would also enhance the chloride resistance of the concrete and make it less prone to corrosion associated with the marine environment [31, 32]. Chloride ions exist in seawater and can permeate the concrete, destroying the passive layer at the surface of the concrete reinforcement. This begins once the chloride concentration reaches a certain threshold and leads to continuous corrosion of the embedded steel [33]. Previous research [33, 34] has shown that increased GGBS replacement levels can lessen the probability of chloride induced corrosion.

Firth et al. [35] have also investigated other approaches such as enhancing the topographical complexity at a different scales and increasing the range of habitats present. Surface texture, holes, cracks pits and pools have been proven to have a significant and direct effect on increasing biodiversity on artificial marine infrastructures [22, 36, 37, 38]. Other research [39] has shown that green algae colonization on the rough surface of 75 cm x 50 cm slabs is faster than for smoother surfaces.

The concept of applying ecological principles to marine infrastructure has only developed within the last decade and to date has been rarely implemented in many coastal environments [40]. It is important to understand the ecology of developed shorelines and to find ways to decrease the impact of urban development. Although some research has been conducted on the use of concrete as a new habitat for marine micro inhabitants [27, 40], they rarely consider the engineering requirements and focus instead on ecological aspects. This paper describes a collaboration between ecologists and engineers to develop concrete materials which could fulfil the structural requirements and further enhance biodiversity on artificial structures. We examine the feasibility of facilitating the growth of marine species on reinforced concrete structures by changing concrete mix design and composition. In addition to testing the engineering characteristics of a range of alternative concrete mixes, we tested whether variation in the aggregate, binder and plasticiser in concrete tiles would affect (a) strength, chloride resistance and alkalinity (b) biological colonisation of tiles deployed on an artificial rocky shore north of Dublin. We also explored the potential for variation in environmental context to alter the influence of concrete composition on biological colonisation.

2. Materials and Methods

A series of mixes were designed to meet the engineering and ecological requirements. The focus of this paper is the influence of mix parameters on the

concrete characteristics, and how these then correlate to environmental performance. This was assessed by designing eight different concrete compositions, and the parameters of interest were binder type, aggregate type and influence of plasticiser.

2.1 Concrete mix design

As the concrete tiles will not be fully submerged and subjected to spray and inter-tidal conditions and corrosion arising from sea-borne chlorides, the Eurocode exposure class was considered to be XS3. For this particular exposure class, the designed concrete tiles will fulfil the Irish National Annex to EN206 requirements. Two binder compositions were used: 100% CEMI, and a 50% blend of CEMI and GGBS. This was selected as it was considered that it would provide a higher chloride resistance, as well as promoting a significant change in concrete alkalinity that could influence marine colonisation. CEMI was selected, as it contains relatively high percentage of C_3A phase (9.5% by weight of binder), which plays a main role in binding of the chloride ions [41]. The coarse aggregates chosen were limestone and granite. Limestone is the dominant aggregate type in Ireland and significant quantities of concrete are manufactured using this. Granite was also chosen to be used as a variable for the field testing. The granite was crushed to a particle size of 10 mm. Finally, a polycarboxylate (PCE) based plasticiser was also added as a variable and the selected dosage was 0.8% of cement content. Plasticiser is routinely added into

concrete mixes to improve the workability. The plasticiser will not have any major influence on the engineering performance, but its influence on colonisation behaviour is completely unknown. A full list of the selected mixes is described in Table 1.

Table 1: Concrete mix design compositions

Mix	***Binder***	***Aggregate***	***Additives***
1	CEMI	Limestone	Plasticiser
2	CEMI	Limestone	None
3	CEMI	Granite	Plasticiser
4	CEMI	Granite	None
5	CEMI + GGBS	Limestone	Plasticiser
6	CEMI + GGBS	Limestone	None
7	CEMI + GGBS	Granite	Plasticiser
8	CEMI + GGBS	Granite	None

The samples manufactured for each designed mix were:

- 3 concrete cylinders of diameter 100 mm and height 200 mm for assessing resistance to chloride ingress and concrete alkalinity.
- 6 concrete cubes of dimension 100 mm for compressive strength testing.

- 8 reinforced concrete tiles of dimension 200 x 200 x 40 mm; these would be later installed in a marine environment and inspected at intervals for colonisation.

All samples were demoulded after 24 hours.

2.2 Engineering characterisation

The compressive strength of the concrete was obtained by testing according to Eurocode method for hardened concrete (EN 12390-3) [42]. The chloride resistance was determined using the Nordtest non-steady state chloride migration test according to NT Build 492 [43]. The test involves driving chloride ions through a concrete section of 100 mm diameter and 50 mm thickness under the action of an electric field. After a pre-determined time (24 hours), the sample is split and sprayed with a 0.1M silver nitrate solution. The penetration depth is measured, and the effective diffusion coefficient is calculated. It should be noted that the diffusion coefficient is a time dependent parameter and may change considerably over time [44]. In this context the use of an age factor, m, is recommended; a value of 0.17 is chosen for the CEMI concretes and 0.06 for GGBS concretes. The use of these equations is shown in Equations 1 and 2.

$$C(X,t) = C_{sn}\left[1 - \text{erf}\left(\frac{X}{2\sqrt{D_m t}}\right)\right] \quad (1)$$

where C_{sn} is surface chloride concentration and coefficient for the exposure time, t, and calculated from Eq. 2 and 3.

$$D_m(t) = \frac{1}{t}\int_0^t D(\tau).\, d\tau \quad (2)$$

$$D(\tau) = D_R(\frac{t_R}{t})^m \quad (3)$$

Where D_m is the mean effective chloride diffusion over the chosen time period, t (50 years); D_R is the chloride diffusion coefficient (determined from testing) at a reference time, t_R, (the timing of in this test, 81 days). To ascertain the real effect of the chloride diffusion coefficient, it is more illuminating to determine the chloride concentration at the rebar level. For this purpose, it is assumed that the rebar has 5cm cover and the exposure period is 50 years. Equations 1, 2 and 3 were then used to predict chloride concentration after 50 years exposure. A surface chloride concentration of 0.8% by mass of binder was assumed; this was based on research by Poulsen and Sørensen [45] who assessed 34 years old concrete bridges in a marine environment. It is recognised that the surface chloride concentration is a time and material dependent parameter, but the use of a fixed value is considered appropriate for comparative purposes. The determination of effective diffusion coefficients based on migration testing is as described by Luping and Nilsson [46]. A chloride concentration of 0.4% is generally considered enough to initiate corrosion. As an alteration in the pore structures is under consideration in terms of cement hydration progress, the above model is considered appropriate for marine environments [33, 47].

Concrete alkalinity was also of interest in this study and this was expressed through the concretes acid neutralisation capacity. This was previously utilised by Glass et al.[48] and involves testing powder samples of the concrete. For this test 16 samples of powder, each weighing 5g, were held in sealed tubes so as to minimise carbonation. For each sample, 5ml of deionised water was added to the concrete and mixed in a 25 ml centrifuge tube. After 24 hours, a variable quantity (ranged from 0.2-5 ml) of 2.5 M nitric acid is added to each sample, along with more water. Using this approach, the total volumes added are adjusted so as to produce 11 ml of liquid in the centrifuge tube. The tubes were agitated daily until the pH of the solution has reached a steady state; in this study the reported measurements are after 10 days. The pH was measured in each centrifuge sample using a pH probe calibrated using standard buffer solutions. Once the relation between pH and quantity of acid added to the sample (expressed in moles / kg of concrete) was obtained, the acid neutralisation capacity (ANC) was measured by the concentration of the acid added to the suspension (ΔC) divided by a change in the pH values (ΔpH) against ΔC [30]:

$$ANC = \frac{\Delta C}{\Delta pH} \tag{4}$$

The height of the plotted spectrum corresponds to the alteration in acid added per unit of induced pH change. The area between any two pH values under the spectrum showed the required quantity of acid to induce the corresponding change in pH [49]. A higher ANC value is indicative of a higher resistance of the

mix against acidification and faster corrosion. The ability of concrete to resist the pH fall influences the inhibitive properties affecting carbonation and the quantity of chloride required to start corrosion of reinforcement in concrete [49].

2.3 Comparing colonisation of different concrete mixes

The concrete tiles were deployed on the breakwater at Mornington, County Meath, on Ireland's Eastern coast (53.720979° -6.240756°). The bio-fouling organisms found at this site are typical of those expected to colonise marine hard sub-strata in North Western Europe. Tiles were attached vertically with a seaward aspect to exposed and sheltered surfaces of the breakwater in April 2018. Tiles were arranged in a random sequence on the mid to low shore of the breakwater, with 6 replicates of each tile type placed on the sheltered side of the breakwater (a total of 48 tiles) and 2 replicates of each tile placed on the exposed side of the breakwater (a total of 16 tiles). This enabled an initial exploration of the potential for variation in environmental context to influence the responses to biological communities to variation in concrete mixes.

After 1 month, the proportions of diatoms, cyanobacteria and green algae within the biofilm were recorded with a Benthotorch. The BentoTorch™ (bbe Moldaenke, Germany) quantifies the intensity of chlorophyll fluorescence of algal, diatom and cyanobacterial cells using emitted light and gives output

biomass values for each biofilm component in the field. On each tile, 5 recordings were taken in an “X” shaped arrangement on the face of the tile, with 4 measurements being taken in each of the corners of the tile and one being taken centrally. This ensured representative sampling of biofilm constituents across the face of the tile. In addition, the tiles were photographed and barnacle abundance was quantified using ImageJ software.

A **B** **C**

Figure 1(A-C): A tile deployment, **B** colonisation of a tile after 1 month and, **C** biofilm sampling using a Benthotorch

2.3.1 Statistical analyses

The data collected after one month was analysed with PERMANOVA in Primer V7 [50], using Bray-Curtis similarity with 10,000 permutations. The factors and levels used in this experiment were as follows: binder (100% CEMI or 50%CEMI / 50% GGBS), aggregate (granite or limestone) and plasticizer (P+ or P-).For each response variable at each time of sampling, two separate analyses were done. The main analysis compared concrete types on the sheltered site (n=6) and an

additional analysis was done for the data from the exposed site (n=2). In all analyses, pairwise tests were used to determine which factors or combination of factors differed significantly from each other. Monte Carlo tests were also used with repeated random sampling of data to account for low numbers of permutations [50]. In all cases the data was untransformed.

3. Results

3.1 Compressive strength

The average compressive strength of the various concrete mixtures was determined at 7 and 28 days and these are presented in Figure 2. It can be seen that higher strengths are generally associated with the limestone aggregate / CEMI concretes, and that the use of GGBS had little effect on the strength.

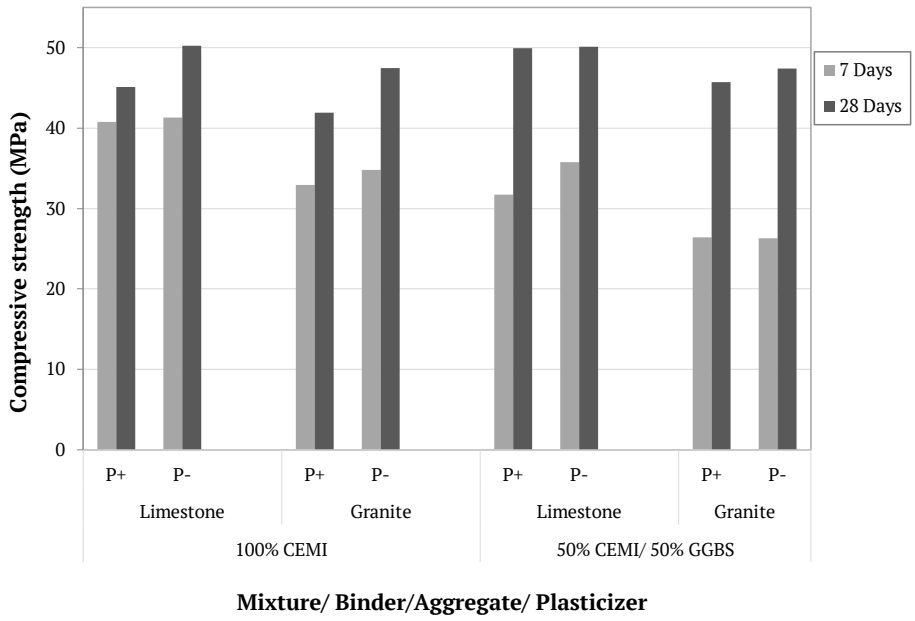

Figure 2: Compressive strength of the various concrete mixes

3.2 Resistance to chloride ingress

The results of the non-steady state migration test are presented in Table 2, leading to a series of non-steady state migration coefficients (D_{nssm}). The highest diffusion coefficients corresponded to the binder combinations containing 100% CEMI binder. The addition of 50% GGBS (for mixes 5 to 8) led to significant reduction in diffusion coefficient in all cases, and this was reflected by a much lower chloride content at rebar level. It was also noted that there was no clear influence associated with the introduction of plasticiser or the variation in coarse aggregate.

Table 2: Results of chloride migration testing

Mix	D_{nssm} ($x10^{-12}$ m^2/s)	D_R ($x10^{-12} m^2/s$)	D_m ($x10^{-12} m^2/s$)	$[Cl^-]$ x = 5cm t = 50 yrs
1	21.5	16.6	4.67	0.54
2	17.1	13	3.66	0.51
3	18.1	13.8	3.87	0.52
4	17.4	13.3	3.73	0.52
5	3.34	2.25	0.41	0.13
6	3.52	2.39	0.44	0.14
7	3.13	2.06	0.38	0.12
8	3.0	1.96	0.36	0.11

3.3 Acid neutralisation capacity

The initial pH for each concrete was reasonably similar, ranging from 12.8 to 13.1 (Figure 3). However, the profiles began to diverge as acid was added. The highest pH was associated with the concretes containing a CEMI binder and a limestone aggregate. When the aggregate is changed to granite there was acceleration in pH reduction; this is associated with the buffering capacity of the limestone aggregate. Similarly, when the binder changes to a CEMI /GGBS blend, there is also a clear drop in acid neutralisation capacity (ANC). The use of CEMI with limestone aggregate (mixes 1 and 2) provided the greatest resistance to a pH

reduction, while the use of a CEMI /GGBS blend and granite aggregate (mixes 7 and 8) provided the lowest. Mixes 7 and 8 also showed to have the best ANC. The use of CEMI /GGBS blend binder showed to have the lowest pH value at which the strongest peak occurred.

It is interesting to note that although the initial pH of each sample is quite similar, there is a significant difference in the reserves of alkalinity associated with each mix. This can be determined by the quantity of acid required to reduce pH of the suspension to a target pH level (e.g. 12, 11 or 10). This data is extracted from titration curves (Figure 3) and presented in Figure 4, where the greatest resistance to a pH reduction and high ANC of the CEMI binder / limestone aggregate can be clearly seen. This parameter is used for subsequent correlation with ecological performance.

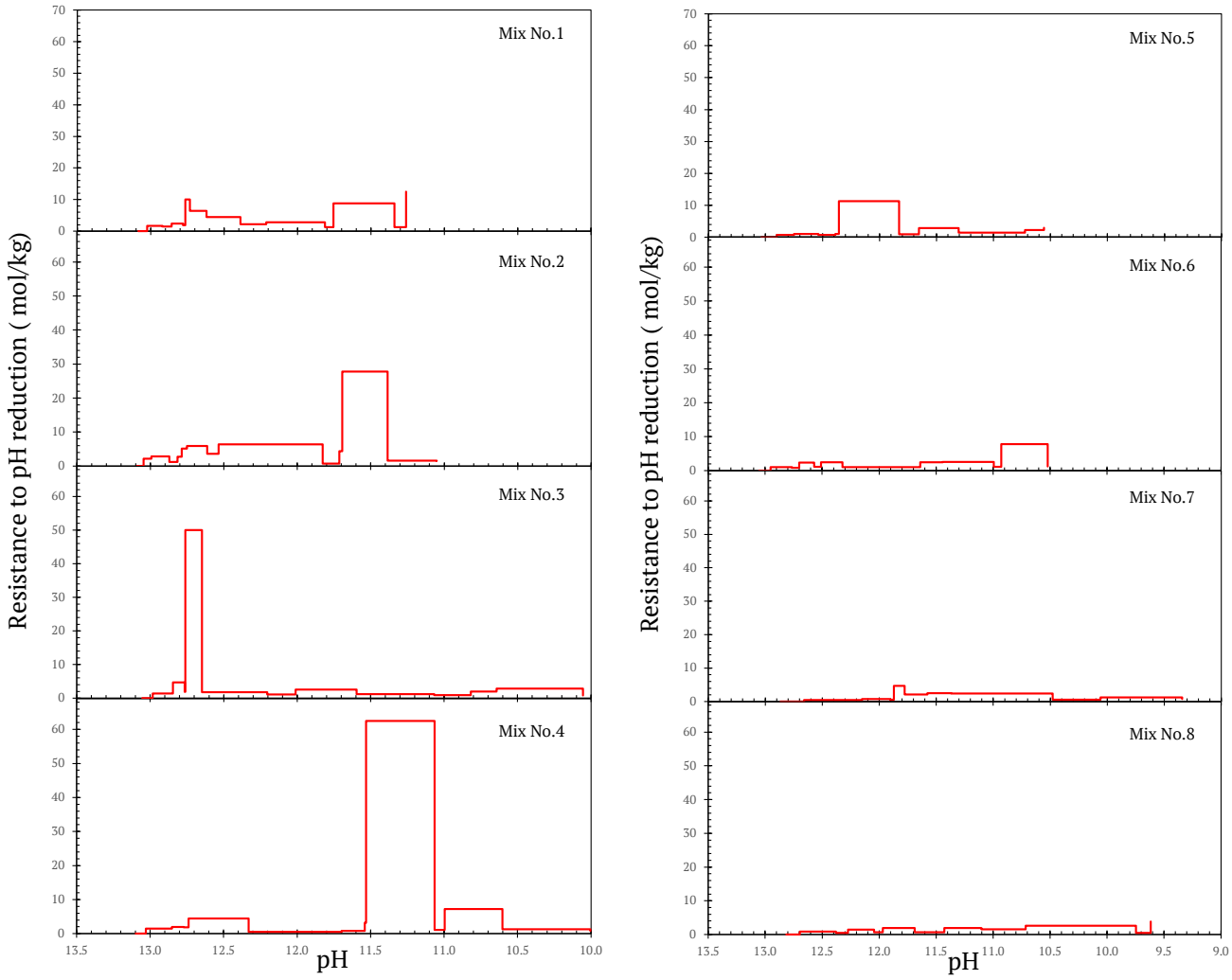

Figure 3: Acid neutralisation profile for each mix

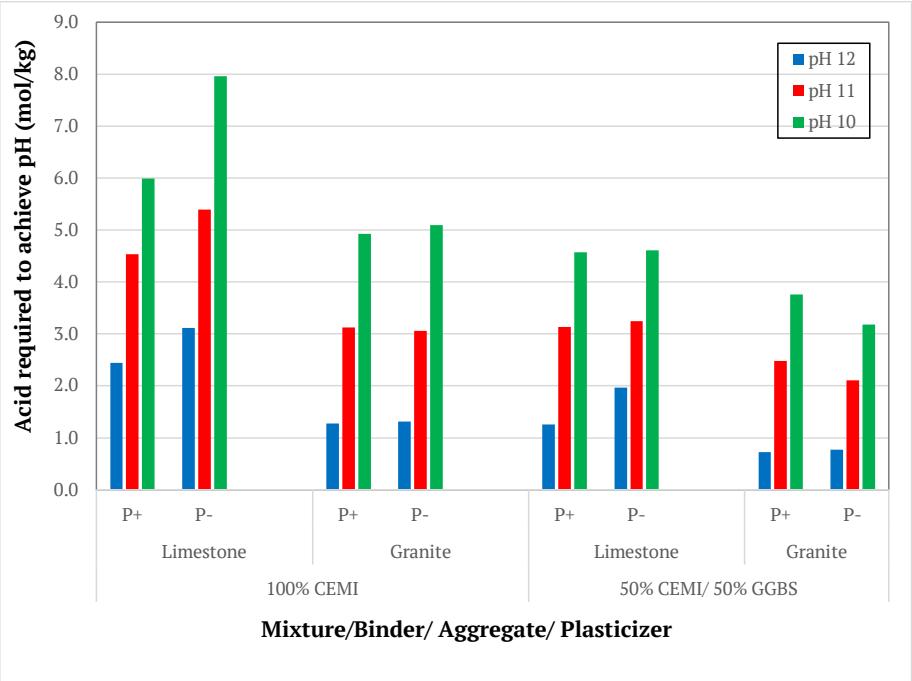

Figure 4: Acid required to achieve a specific pH for each mix (expressed as moles of acid / kg of concrete)

3.4 Biofilm and epibiota

On the sheltered side of the breakwater, the biomass of diatoms, cyanobacteria and green algae on tiles was influenced by binder composition. For example, the tiles with a 50%CEMI / 50%GGBS blend had significantly higher biomass of diatoms compared those tiles with 100% CEMI binder (Figure 5A-C; Table 3 A-C; Table 4 A-C).

Overall tiles deployed on the exposed side of the breakwater showed distinctly reduced biomass of diatoms, cyanobacteria and green algae compared to the tiles deployed on the sheltered side. Although there appeared to be higher

cyanobacteria biomass on tiles with 50% CEMI / 50% GGBS binder of limestone aggregate without plasticizer in exposed environments, this was not significant due to considerable variability being observed around this mean. Diatom biomass was significantly influenced by combinations of binder and aggregate in which tiles with 50% CEMI / 50% GGBS binder and limestone aggregate had significantly greater biomass of diatoms compared to tiles with 100% CEMI binder and limestone aggregate (Figure 5A; Table 3A; Table 4D). Tiles with a 50% CEMI / 50% GGBS binder had significantly higher biomass of cyanobacteria compared to tiles with a 100% CEMI binder (Figure 5B; Table 3B; Table 4E). Lastly, green algal biomass was influenced by several combinations of binder, aggregate and plasticizer (Figure 5C; Table 3C; Table 4F-I).

On tiles deployed in the sheltered site, barnacle abundance was influenced by a combination of binder, aggregate and plasticiser (Figure 6A; Table 3D) where there was significantly higher abundance of barnacles on tiles with 50% CEMI / 50% GGBS binder, granite aggregate and plasticizer compared to tiles with 100% CEMI binder, granite aggregate and plasticizer (Figure 6A;Table 4J). In addition, tiles with 50% CEMI / 50% GGBS binder and granite aggregate, with plasticizer had significantly higher abundance of barnacles compared to tiles with 50% CEMI / 50% GGBS, granite aggregate without plasticizer (Figure 6A;Table 4K). On exposed tiles there appeared to be an interaction between aggregate and plasticizer, however, post hoc tests failed to unravel these means (Table 3D ;Figure 6B).

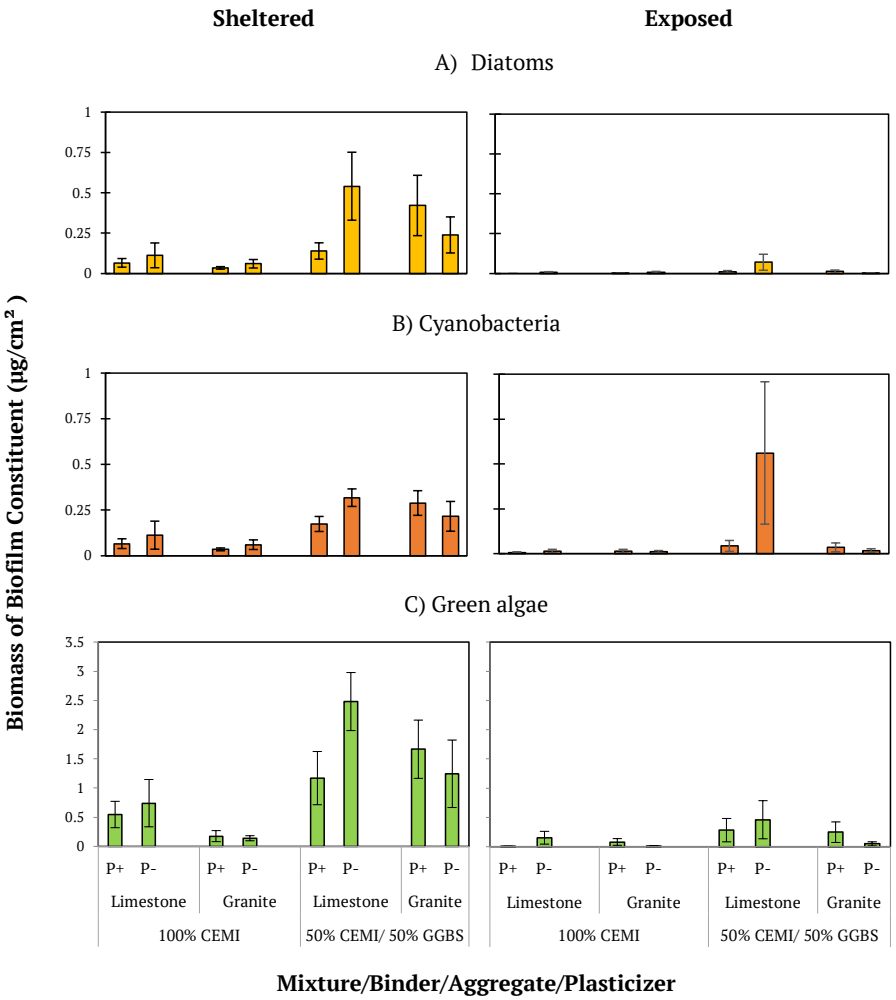

Figure 5(A-C): Biomass of A) diatoms, B) cyanobacteria and C) green algae on tiles with varying levels of binder, aggregate and plasticizer in a sheltered and an exposed environment. (Note: P+/ P- represents presence or absence of plasticizer; the axis scale for green algae differs from other graphs).

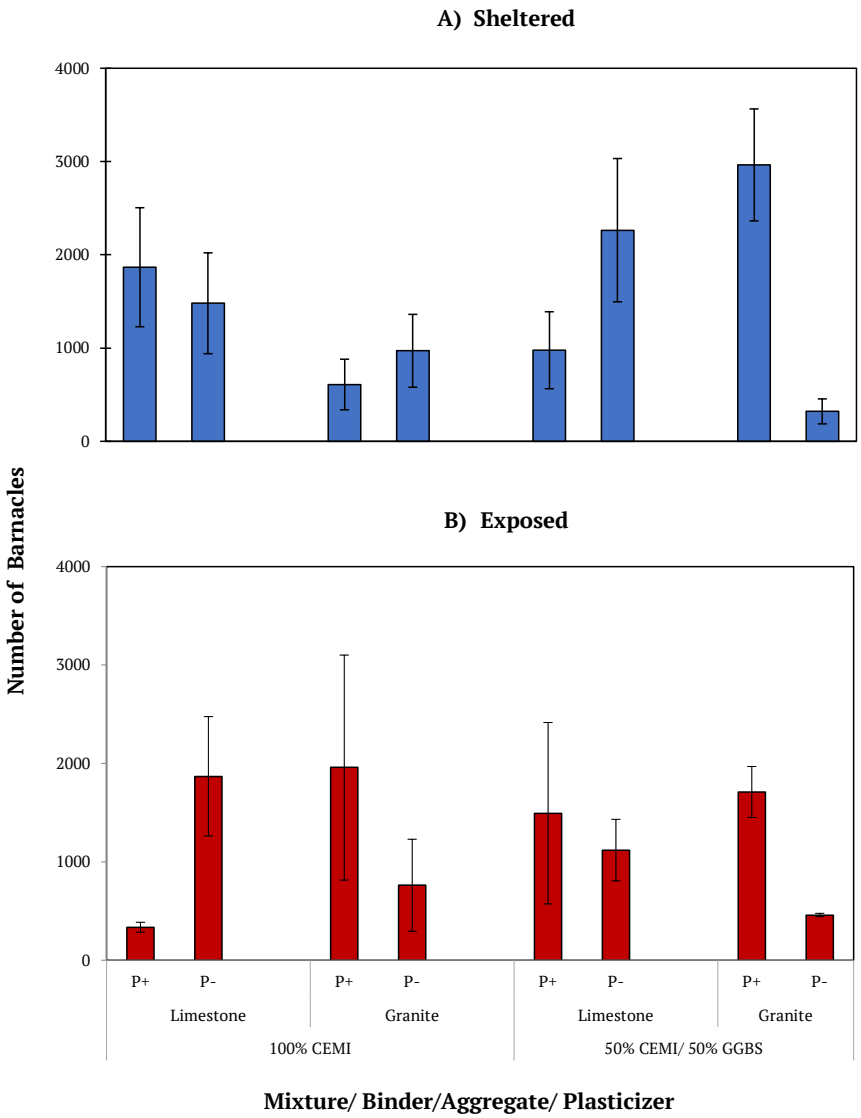

Figure 6 (A-B) Barnacle abundance on tiles with varying levels of binder, aggregate and plasticizer in A) sheltered and B) exposed environments. (Note: P+/ P- represents presence or absence of plasticizer) . For sheltered tiles n=6 and for exposed tiles n=2.

Table 3: PERMANOVA analysis of the abundance of A) diatoms, B) cyanobacteria and C) green algae and D) barnacles on tiles with varying binder, aggregate and plasticizer, sampled one month after immersion. Data is untransformed.

Sheltered site (n=6)		**A)**			**B)**			**C)**			**D)**		
Source of variation	**df**	**MS**	**F**	***p*(MC)**	**MS**	**F**	***p*(MC)**	**MS**	**F**	***p*(MC)**	**MS**	**F**	***p*(MC)**
Binder = Bi	1	1231.4	15.53	**0.0003**	28033	23.2	**0.0001**	17186	7.98	**0.001**	1083.8	0.5	0.627
Aggregate = Ag	1	17.5	0.22	0.675	1046.3	0.87	0.42	3802	1.77	0.158	1894.8	0.87	0.41
Plasticizer = Pl	1	41.5	0.52	0.488	1101.6	0.91	0.404	997.7	0.46	0.703	1077.8	0.49	0.628
BixAg	1	18.1	0.23	0.668	219.9	0.18	0.876	577	0.27	0.874	2330.1	1.07	0.331
BixPl	1	31.8	0.4	0.554	272.9	0.27	0.843	1135.4	0.53	0.663	1596.4	0.73	0.474
AgxPl	1	237.7	3	0.093	1913	1.58	0.198	4136.3	1.92	0.137	3328.1	1.52	0.204
BixAgxPl	1	254.1	3.2	0.077	2274.8	1.88	0.153	2241.2	1.04	0.362	9537.8	4.36	**0.018**
Res	40	79.3			1207.5			2152.9			2185.6		

Exposed site (n=2)		**A)**			**B)**			**C)**			**D)**		
Source of variation	**df**	**MS**	**F**	***p*(MC)**	**MS**	**F**	***p*(MC)**	**MS**	**F**	***p*(MC)**	**MS**	**F**	***p*(MC)**
Binder = Bi	1	3.9	7.8	**0.026**	7296.1	10.3	**0.002**	7127.4	11	**0.002**	330.3	0.4	0.66
Aggregate = Ag	1	2.4	4.7	0.06	1823.5	2.57	0.103	3349	5.19	**0.024**	2.5	0.003	0.999
Plasticizer = Pl	1	2.4	4.71	0.061	625.8	0.88	0.424	373.3	0.58	0.585	273.9	0.33	0.695
BixAg	1	2.7	5.32	**0.049**	1380.7	1.95	0.178	713.6	1.11	0.341	348.7	0.42	0.634
BixPl	1	0.7	1.42	0.269	1265.3	1.78	0.19	1262.6	1.96	0.163	2065.7	2.49	0.124
AgxPl	1	2.8	5.64	**0.045**	1817.3	2.56	0.098	9515.3	14.7	**0.001**	5883.9	7.09	**0.016**
BixAgxPl	1	2.8	5.63	**0.043**	1826	2.57	0.104	6057	9.38	**0.002**	495.5	0.6	0.531
Res	8	0.5			709.4			645.6			830.1		

Table 4: Pairwise comparisons

Interaction	Variable	Pairwise comparison	*p* (MC)
A	Diatoms	50% CEMI / 50% GGBS > 100% CEMI	<0.001
B	Cyanobacteria	50% CEMI / 50% GGBS > 100% CEMI	<0.001
C	Green algae	50% CEMI / 50% GGBS > 100% CEMI	<0.01
D	Diatoms	50% CEMI / 50% GGBS + Limestone > 100% CEMI + Limestone	<0.05
E	Cyanobacteria	50% CEMI / 50% GGBS > 100% CEMI	<0.01
F	Green algae	Limestone + 100% CEMI - Plasticizer > Granite + 100% CEMI -Plasticizer	<0.01
G	Green algae	100% CEMI + Granite + Plasticizer > 100% CEMI + Limestone + Plasticizer	<0.05
H	Green algae	50% CEMI / 50% GGBS + Limestone - Plasticizer > 50% CEMI / 50% GGBS + Granite -Plasticizer	<0.05
I	Green algae	100% CEMI + Limestone -Plasticizer > 100% CEMI + Limestone + Plasticizer	<0.01
J	Barnacle spp.	50% CEMI / 50% GGBS + Granite + Plasticizer > 100% CEMI + Granite + Plasticizer	<0.05
K	Barnacle spp.	50% CEMI / 50% GGBS + Granite + Plasticizer > 50% CEMI / 50% GGBS + Granite - Plasticizer	<0.05

4. Discussion

4.1 Concrete characterisation

The focus of the initial concrete testing was to establish that the selected mix designs were appropriate for deployment in the marine environment. The results of the compressive strength testing showed that all candidate mixes achieved this, but with slightly lower strengths for concretes with granite aggregates. This behaviour has previously been reported by Wu et al. [51], although the opposite has also been observed [52, 53]. As expected, the early age strength of GGBS concrete mixes are lower than the CEMI mixes, but this evens off by 28 days. Again, similar behaviour has been reported in the literature [33, 41, 54, 55].

4.2 Concrete alkalinity

The results of the chloride migration testing show the significant positive influence of the GGBS, as mixes 5 to 8 have performed significantly better than the concretes manufactured using a 100% CEMI binder. The influence of aggregate and plasticiser was considerably less. The impact of GGBS was expected, and Kumar et al. [56] has previously noted that GGBS concretes have a denser cement matrix and decreased pore size. The ANC is a key property of concrete mixes, as the resistance to acidic environments can influence concretes durability as well as its leaching behaviour.

There are several solid phases which are responsible for the resistance to acidification, largely associated with the formation of C-S-H compounds. The added acid per unit of pH decrease gives the resistance to the pH reduction or the buffering index [57], and different binders have very different buffering capacity [48]. In our paper, the experimental results have shown that the CEMI /GGBS blends present a lower resistance to pH reduction (Figure 4), as the hydration of CEMI /GGBS blend produces less calcium hydroxide than 100% CEMI blends; this is supported by previous research from Glass et al. [48]. The pH fall influence the level of required chloride to initiate corrosion and breakdown of reinforcement passive film.

Our results in Figure 4 also showed that granite aggregate concretes had a lower ANC than limestone aggregate concretes. This could also be explained by the dissolution of calcium hydroxide which accompanies by the reaction between the limestone aggregate with hydroxyl ions as the pH reduces [29]. The use of a plasticiser did not show any significant effect on the ANC. Together these results show that the concrete alkalinity is controlled primarily by the binder type, with a lower influence coming from the aggregate. This has implications in designing concrete for colonisation by non alko-tolerant species.

4.3 Early biological colonisation

Previous work has highlighted the unsuitability of traditional Portland cement concrete structures as habitats for marine flora and fauna, largely attributed to the

high surface alkalinity of this material [33, 38, 58, 59]. Our results have shown that by manipulating the composition of the concrete mixes it was possible to influence concrete surface chemistry and the early colonization of biofilm and invertebrates one month after deployment. In particular, the concrete mixes manufactured using a CEMI /GGBS binder supported significantly greater biomass of biofilm components (diatoms, cyanobacteria and green algae); this was especially pronounced in sheltered environments. These mixtures also have a lower surface alkalinity, more closely resembling pH values of seawater in this region [60] which likely explains the increasing growth of biofilm on these surfaces. Similar results have been seen in other studies. For example, Nandakumar et al. [58] compared diatom biomass and diversity on pozzolan containing blocks versus standard concrete blocks and showed increased biomass and diversity of diatoms on the lower surface alkalinity pozzolan blocks. Although we did not measure the species richness of diatoms, cyanobacteria and green algae in the current study, the above study suggests that richness may also increase on GGBS based concretes with lower surface alkalinity. Given the importance of biofilm communities in providing chemical cues which induce the settlement of other organisms [17, 61, 62, 63] as well as providing an important food source for grazing invertebrates [64, 65] the addition of GGBS based binders in concrete structures is likely to provide a more resource rich habitat and may influence subsequent colonisation.

On tiles on the exposed side of the breakwater, there was greater variability in the patterns of biofilm colonization compared to those on the sheltered side (Section 3.5.1, Table 3; Figure 5). As was the case on the sheltered side, the biomass of both diatoms and cyanobacteria was significantly higher on tiles with GGBS binder, although in the case of diatoms this pattern was only observed on tiles with also had limestone aggregate. However, green algal biomass varied considerably as biofilm communities were influenced by several combinations of binder, aggregate and plasticiser with the consistent effect of the GGBS binder, observed at the sheltered site no longer being apparent. The greater variability observed on tiles in the exposed site may be explained some extent by the increased environmental variability of wave activity in exposed environments. Although all tiles were attached facing vertically and facing towards the water, the complex features of the breakwater may have led to subtle variation in degree of exposure between individual tiles. This coupled with the lower replication (n=2) for exposed tiles may have contributed to the variability in the observed patterns for green algae. That said, the results from exposed tiles again suggest that the lower acid neutralisation capacity of GGBS based tiles leads to increases in biofilm abundance.

Barnacle abundance was also shown to vary across the tile mixes. Although some consider barnacles to be more alkotolerant than most species [66, 67], our results showed that in some cases, the addition of GGBS leads to a significant increase in barnacle abundance, particularly on tiles which contained granite aggregate and

plasticiser at the sheltered site (Section 3.5.2, Table 4, Figure 6). This again suggests that in some cases lower acid neutralisation capacity concretes which contain GGBS may create more suitable colonization surfaces for crustaceans. In addition, certain mixtures which lacked plasticizer showed significantly higher barnacle abundance compared to the alternative mixture which contained plasticizer. Interestingly, this was also among the patterns observed for green algae biomass on exposed tiles as discussed above (Section 3.5.1). Previous studies have shown that some plasticizers can be toxic to certain forms of algae and invertebrates. For example, Azizian et al. [68] showed that leachate from Portland cement concretes which contained plasticizer resulted in higher growth inhibition and mortality of the freshwater algae (*Selenastrum capricornutum*) and crustacea (*Daphnia magna*) compared to leachate from Portland cement concretes which lacked plasticizer. Even though the above study did not study the specific plasticizer used in our tiles (polycarboxylate), our results also suggest that the presence of plasticizer may influence the colonization of barnacles and algae to some extent. However, as barnacle abundance can be increased on tiles which contain plasticizer as shown above, the extent to which plasticizer effects colonisation is unknown, hence this requires further targeted research.

Although there were distinctive differences in the early colonisation of our concrete tiles on both the sheltered and the exposed side of the breakwater, past studies have shown a tendency for these patterns to homogenise as time progresses [69, 70]. Further study is required to characterise the longer-term effects of variation in

concrete mix and variation in the patterns of initial biological colonisation reported here.

5. Conclusion

In this study, although we clearly show that all of the eight difference concrete mixes that were tested were capable of meeting the requirements of Eurocode 2 (in term of resistance, serviceability, durability) with respect to the selected exposure class. Only the concretes manufactured using a GGBS/CEMI binder were likely to have the required chloride resistance to provide a long service life. These findings will reassure engineers and designers that there are more environmentally- and/or indeed eco-friendly options available that still meet the criteria to ensure the structural integrity of the marine infrastructures. This is particularly important as more of these structures will be required under predicted scenarios for human population growth and in terms of the increase in coastal protection associated with climatic change.

From an eco-engineering perspective this study has highlighted that further cross-disciplinary collaboration between engineering and ecological disciplines is important. Particularly, with regard to the development of materials which are structurally viable for use in coastal infrastructure, as well as being more receptive to colonisation by marine epibiota. This study also highlights that the early ecological performance, assessed by monitoring biofilm and barnacle colonisation, is crucial in the selection of the most appropriate mix design but this work needs to be expanded

into testing those designs over longer temporal scales and in different environmental contexts. Here we showed that certain mixes had a clear influence on biofilm development on the sheltered side of the test site but on the exposed side of our study site , the performance was not so clear. Such collaborations and expansion of the work undertaken here within this study will broaden our knowledge and better inform the design of interventions in ecological engineering. Thus, increasing the potential to reduce the ecological impacts that artificial structures have on marine ecosystems.

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