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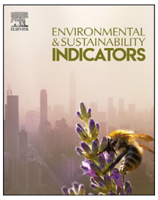

The study of long-term durability and bio-colonization of concrete in marine environment

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ABSTRACT

The purpose of this paper is to study the long-term durability and bio-colonization of concrete in marine environment. In this work, concrete formulations were developed and optimised by varying the type of cement (CEMII and CEMV) and introducing shellfish by-products (Oyster Shells) into their composition (by substituting 20% by weight of 4/10 aggregates). Four concrete formulations were thus studied.

The durability of these materials upon bio-colonization were tested after 90 days, 180 and 360 days of immersion in natural seawater. The monitoring of the photosynthetic activity of biofilms and the biomass on the materials surface showed a better acclimatisation of the microphytobenthos in CEMII 20% Shells concrete than in other concretes despite a lower colonization on this concrete. It was also noticed that the chlorophyll biomass was the highest in concrete CEMV 20% Shells after 360 days. During immersion, the mechanical strengths of CEMII 0% Shells, CEMII 20% Shells and CEMV 20% Shells increased. At long term of immersion, the chloride ions diffusion was more reduced, in natural seawater, for CEMII 0% Shells, CEMII 20% Shells and CEMV 20% Shells concretes than for concrete CEMV 0% Shells. these results lead to the assumption that the accumulation of biofilm plays a role as protective barrier against the action of chloride ions. Finally, it appears that the concrete CEMII 20% Shells is the most suitable concrete mix design for marine infrastructure amongst the tested designs.

1. Introduction

Coastal areas play a crucial role in the economic, social and political development of most countries. As a result, the maritime coasts are increasingly urbanized. Indeed, human activities (ports, tourism, fishing …) require maritime structures and infrastructures which are often made of concrete. These coastal developments are responsible for the loss of many marine species habitats (Firth et al., 2013, 2014). It is therefore important to offset such impacts by generating an equivalent gain in biodiversity.

This study is carried out within the framework of the European Marineff project, which partially targets this context. One of its objectives is the design of maritime infrastructures for flat oysters (*Ostrea edulis* Linnaeus, 1758) restoration in the Channel. Indeed, the European flat oyster is an endangered species. This species is also considered as an ecosystem engineer. According to Jones et al. (1994), ecosystem engineers are "*organisms that directly or indirectly modulate the availability of resources to other species, by causing physical state change in biotic or abiotic materials*". The implementation of so-called biomimetic infrastructures is to be favoured in order to lead to a natural process in which these species allow the creation of new habitats.

Cementitious materials are bio-receptive in the marine environment. Guillitte (1995), defines the concept of bioreceptivity as "*the ability of a material to be colonized by one or more groups of living organisms without necessarily inducing bio-deterioration*". Bioreceptivity depends on the intrinsic properties of the cement matrix such as porosity and roughness (Ammar et al., 2015; De Muynck et al., 2009; Manso et al., 2015).

Over the years, a new approach has emerged, in the aim of enhancing marine infrastructure by varying surface condition (smooth or rough), structure, orientation or/and composition to promote ecological succession (Firth et al., 2014; De Muynck et al., 2009; Glasby, 2000; Ly et al., 2020; Perkol-Finkel and Sella, 2014; Sella and Perkol-Finkel, 2015). Indeed a modification of the material can have an impact on the recruitment of many intertidal marine organisms. Thus, the term "ecological engineering" emerged (Firth et al., 2014, 2016; Bergen et al., 2001; Dennis et al., 2018; Pioch et al., 2018; Strain et al., 2018). The

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effectiveness of eco-engineering interventions varies according to habitats and marine biological communities. Indeed, each marine organism has a different response depending on the infrastructure (Jones et al., 1994; Coombes et al., 2015; Hanlon et al., 2018; Vivier et al., 2021).

One of the solutions could therefore be the design of bio-receptive and sustainable concrete for the implementation of these infrastructures. Concrete immersed in the marine environment will undergo chemical (Jakobsen et al., 2016; Yi et al., 2020), physical (Mehta, 2019) and biological attacks that can lead to its deterioration (Bastidas-Arteaga et al., 2008; Chlayon et al., 2020; Cwalina, 2008; Jayakumar and Saravanane, 2009, 2010; Sanchez-Silva and Rosowsky, 2008). It is therefore important to design concrete that is as durable as possible in order to ensure its sustainability in its immersion environment.

This study aimed to develop and optimize concrete formulations and select the most suitable for marine infrastructure manufacturing. For that purpose two types of cement were used and a partial substitution of natural gravels by shell aggregates (mollusc shells from oyster species) has been carried out. In order to determine which concrete mix design is the most bio-receptive, the surface colonization was studied using a Junior Pam. Durability tests such as chloride ions diffusion were also conducted on immerged samples to determine which concrete mix design is the most sustainable.

2. Materials and methods

To study concretes' durability and bio-colonization in marine environment, two types of 11 cm diameter cylindrical samples (5 and 22 cm in height) were elaborated and subjected to chloride ions diffusion and compressive tests (Fig. 1). Slump and entrapped air tests (NF EN 12350-2, 2019; NF EN 12350-7, 2019) were operated during optimization of the different concrete design. Once optimization finished, the manufacturing of the different concrete mix design was under taken. After demoulding, the specimen were cured in controlled room for 90 days at 100% of Relative Humidity (RH) and at temperature of 19 °C. At this stage, thermogravimetric and compressive strength measurements were practiced on one third of the samples, as a reference state, while the remaining samples were immersed in either Artificial or Natural Sea-Waters (ASW and NSW respectively). After 90, 180 and 360 days of immersion, colonization monitoring, compressive strength, chloride ion profiles and thermogravimetry measurements were carried out on each sample.

Before the concrete mix design optimization, physical tests were conducted to characterize the raw material (Table 2). The absolute density of oyster shell aggregates is 2725 kg.m^{-3} (NF EN 1097-6, 2014). Their water absorption coefficient (4.58%) (NF EN 1097-6, 2014) is high compared to other aggregates used for concretes. The Granular compactness was also determined (NF EN 932-2, 1999). The mix design is optimised for environmental exposition XS3 (NF EN 206+A1, 2016). The obtained concrete formulations are presented in Table 3.

2.1. Concrete's formulations

For this study, 4 concrete mix were designed with 2 types of cement (Calcia), CEMII/A-LL 42.5 R CE PM-CP2 NF and CEMV/A (S–V) 32.5 N-LH CE PM-ES-CP1 NF. These types of cement are suitable for marine environment applications. Their chemical compositions is given in Table 1.

A siliceous alluvial 0/2 mm sand was used. Alluvial aggregates were also used and are composed of sandstone and quartz, with two main mean sizes of 4/10 mm and 10/20 mm (Fig. 2). We operated a substitution of 20% of the 4/10 mm aggregates mass with oyster shell aggregates (6/12 mm) in order to study the effect of this biomineralized by-product on potential oyster larvae recruitment. Indeed, different studies demonstrated that an introduction of seashell aggregates into concrete composition favors their bio-receptivity by providing an ideal substrate for the settlement of marine organisms (Hanlon et al., 2018; Graham et al., 2017). However, to maintain sufficient mechanical strengths, ground seashell can replace not more than 20% of fine aggregates in concretes (Eziefula et al., 2018; Cuadrado et al., 2016a).

2.1. In situ experimental set-up

After 90 days of curing at 100% of RH, samples were placed in cages made of iron grids (Fig. 3a) and then placed in the Rance river close to Dinard (GPS 84 : 48°655224/2°061009, France) in June 2019 (Fig. 3a). The immersion site is situated at the Rance Bay which is influenced by the marine tidal currents (Axe North/South) enforced by Rance Estuary dam's. The biological diversity of the bay consists of different species of macroalgae (mainly Rhodophyta and Heterokontophyta), Porifera and Mollusca (Gallon et al., 2013).

After 90 days of immersion (September 2019), another set of samples were recovered and placed in semi-enclosed mesocosms (tanks filled

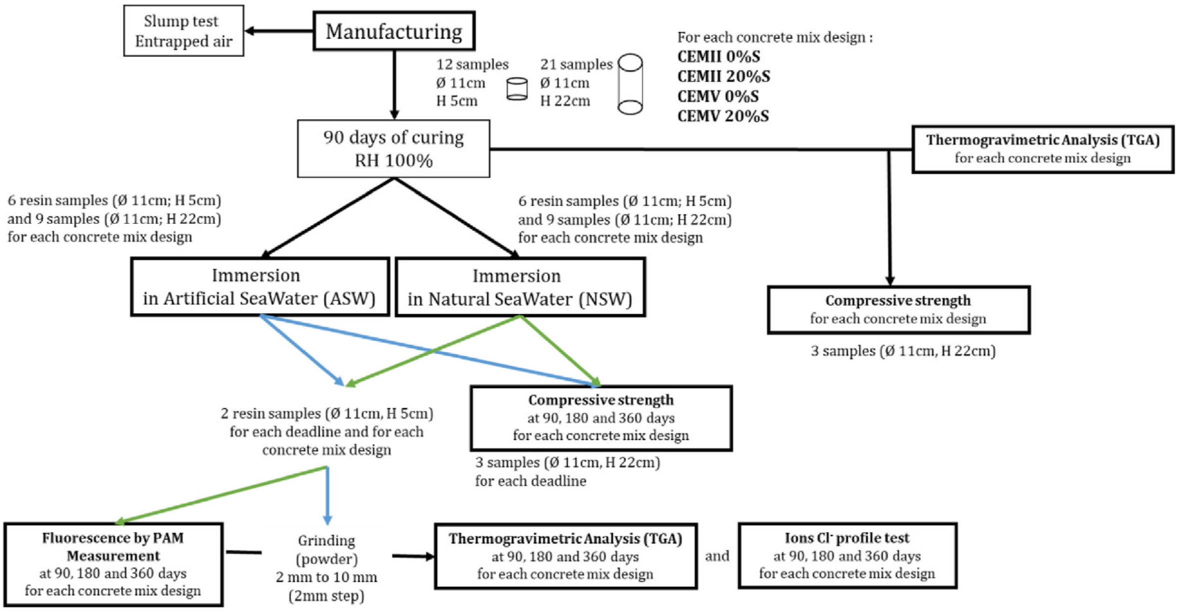


Fig. 1. Experiments set-up of research work.

Table 1
Chemical oxide contents in % of the studied cement (Calcia).

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	S^-	Cl^-
CEMII	19.4	4.5	3.8	0.3	0	63.7	1	2.6	0.86	3	0.3	0.1	0.03
CEMV	30.3	10	3.9	0.5	0.1	46.3	2.5	3.0	0.99	0.32	0.3	0.25	<0.007

Table 2
Characteristics of used aggregates.

Aggregates Characteristics	Sand 0/2 mm	Gravels 4/10 mm	Gravels 10/20 mm	Oyster shells 6/12 mm
Absolute density (kg.m^{-3})	2740	2699	2704	2725
Water absorption coefficient WA24 (%)	0.54	0.62	0.79	4.58
Granular compactness (%)	66	58	58	38

Table 3
Concrete's formulations (in kg/m^3 of concrete).

Formulations Components	CEMII 0% Shells	CEMII with 20% shells	CEMV 0% Shells	CEMV with 20% shells
Cement	350	350	350	350
Sand	800	800	800	800
Gravel 4/10	600	479	600	479
Gravel 10/20	500	500	500	500
Shell	0	121	0	121
Water	175	175	175	175
Superplastifier	4.50	7	4.50	7

with circulating seawater, Fig. 3b) for additional 90 and 270 days (corresponding to 180 days and 360 days immersion in NSW). These mesocosms are installed at the CREC-Unicaen Marine Station in Luc-sur-Mer (France). The NSW is directly pumped from the Seine Bay into the tanks. It is collected by the marine station using an intake installed in the subtidal area of the bay and passes through a 20 μm filter. This system allows the development of macro-algae and other micro-organisms.

For ASW condition, samples were immerged in tanks containing Artificial SeaWater made from salt Instant Ocean©, Spectrum Brand dosed at 33.3 g.L^{-1} (Atkinson and Bingma, 1997). These samples will make it possible to distinguish the effect of seawater chemical attack from the effect of bio-colonization on the concrete durability.

2.2. *Tests for concrete durability under marine environment*

2.2.1. *Compressive strength*

The compression tests were carried out on the 11 × 22 cm cylindrical samples using a 3R press (4000 kN) after 90 days of curing (reference concrete) and after 90, 180 and 360 days of immersion in NSW and in ASW. The tests were operated in accordance with the NF EN 12390-3 standard (NF EN 12390-3, 2019).

2.2.2. *Natural chloride ions diffusion*

In order to measure the chloride ions diffusion into concrete, 11 × 5 cm cylindrical samples were immersed in NSW and in ASW for 90, 180 and 360 days. Before immersion, an epoxy resin was applied to the side surface and the bottom of the samples to ensure the direction of diffusion in the specimen (resin-coated samples) (Fig. 1). The exposed surface corresponds to the smooth one without resin.

Ion chromatography was used to measure chloride ions concentrations for a total depth of 1 cm into the samples (using a 2 mm step). The chloride ions diffusion monitoring was realised following a specific protocol. The chloride ions were extracted from the powder produced by grinding. The extraction is carried out by dissolving this powder in ultrapure water and filtrating the leachate. The obtained solution is diluted in a 50 mL flask. The final solution was analyzed by an 883 Basic Ion Chromatograph using standard preparation procedures.

Fig. 2. The various types of aggregates used to elaborate the concrete of this study.

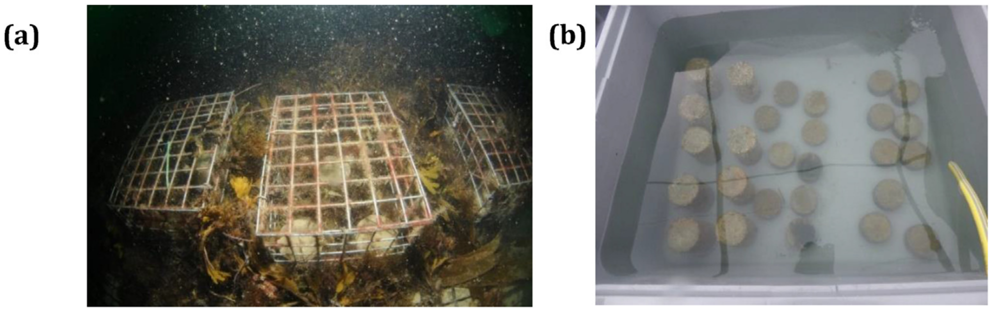


Fig. 3. a): immersion of concrete specimens for 90 days in NSW (Dinard Bay, France) and **b)**: their subsequent immersion in NSW mesocosms.

The monitoring of the penetration of free Cl^- ions was carried out on one sample for each concrete mix design.

2.2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analyses provide information on the evolution of the material mineralogical composition. These analyses were carried out using an STA 449 F5 (Netzch). Tests were performed over a temperature range of 20 °C–1000 °C, with a heating rate of 10 °C/min and a 50 mL/min nitrogen sweep. These tests were carried out on powder specimens obtained from the grinding of the surface layer (0–2 mm) of reference concrete (after 90 days of curing) and on the immersed samples (NSW and ASW).

2.3. Colonization monitoring by PAM measurements

Photosynthetic parameters of the biofilms were assessed using Pulse Amplitude Modulation (PAM) measurements. The quantum efficiency of the photosynthetic charge separation (F_v/F_m) is widely used as an indicator of the nutrient stress of microphytobenthos cells (Juneau et al., 2005). To perform these measurements, a Junior PAM (Walz Teaching-PAM fluorometer) was used. The fluorometer is connected to the sample by a single plastic fibre (50 cm long and 1.5 mm in diameter). After 10 min of dark acclimation which was sufficient for the oxidation of the Quinone A (Q_A) pool, the measurement of the photosynthetic parameters is performed directly on the material surface.

The sample was excited by a weak blue light (1 μmol.photons.m^{-2}.s^{-1}. 450 nm, 0.6 kHz) to record minimum fluorescence (F_0). The F_0 is an index of the chlorophyll biomass. It is expressed on the basis of arbitrary units of relative absorbance (a.u). Maximum fluorescence (F_m) was obtained during a saturating light pulse (0.6s, 1500 μmol.photons.m^{-2}.s^{-1}, 450 nm) allowing all the Quinone A pool to be reduced. F_v/F_m was calculated according to Genty et al. (1989) (equation (1)):

$$\frac{F_v}{F_m} = \frac{(F_m - F_0)}{F_m} \tag{1}$$

The samples were exposed to nine irradiances (E) from 0 to 420 μmol photons m^{-2} s^{-1} for 80 s at each step. Thus, steady-state fluorescence (F_s) and maximum fluorescence (Fm') were measured for each irradiance. The relative ETR (Electron Transport Rate) is calculated according to equation (2):

$$rETR(E) = \frac{F_m' - F_s}{F_m'} \times \mathrm{E} \tag{2}$$

To estimate the photosynthetic parameters, the rETR values were plotted as function of E. The mechanistic model developed by Webb et al. (1974), applied to fit the data to estimate α (μmol electrons.(μmol photons^{-1}) and Ek (μmol photons.m^{-2}.s^{-1}) with α the initial slop of the FLC and Ek the light saturation index (equation (3)):

$$rETR = \alpha \times \mathrm{Ek} \quad \times \left(1 - e^{-\frac{E}{Ek}}\right) \tag{3}$$

Then the maximum of relative Electron Transport Rate ($rETR_{max.}$ μmol electrons.m^{-2}.s^{-1}) is calculated in accordance with equation (4):

$$rETR_{MAX} = \alpha \times Ek \tag{4}$$

The measurements were carried out on triplicates on the mortar surface (11 × 5 cm cylindrical samples) (Fig. 1). The average of triplicates allows to obtain an estimation of the biofilm photosynthetic capacity.

3. Results and discussion

3.1. Colonization of the different concrete mix designs

After only 90 days of immersion in NSW, all the samples exhibit colonization by sessile fauna and some macroalgae. We could count some bryozoans, sponges, serpulid and spiral tubes of Spirorb on the 11 × 22 cm cylindrical samples. At this immersion stage, the measurements of the photosynthetic activity of the biofilm were not carried out on the 11 × 5 cm cylindrical samples due to the low colonization by micro-phytobenthos. The fluorescence signal was too much weak, due to sedimentation on the concrete specimens (Fig. 4a). Some larvae of flat oysters (*Ostrea edulis*) were fixed on a few samples (Fig. 4a). The disparity of this fixation on the different concretes does not indicate which formulation is the most favourable for the recruitment of this species. However, it is interesting to observe the behaviour of the material following the accumulation and growth of marine species attached to its surface such as Risinger (2012) demonstrated a better strength in part to the biological oyster growth over time that encapsulates the concrete.

For longer immersion times and as early as 180 days, including 90 days *in situ*, many species of macroalgae have developed on the concrete specimens surface (Fig. 4b) with mainly macroalgae of the genus *Ulva*. The studied long-term period allowed to show the seasonality impact on the material bio-colonization and on the biofilm photosynthetic parameters which depend thus on the environmental conditions (temperature, light intensity, nutrients …).

The chlorophyll biomass index F_0 after 180 and 360 days of immersion (Fig. 5a) clearly shows that all concrete samples have been colonized. Furthermore, for each type of cement (CEMII or CEMV) regardless of the aggregate type (whether with or without shellfish incorporation), concrete does not show the same bio-colonization at long term. The obtained results show that F_0 values varies according to cement type for the different concrete mix designs. The F_0 values after 180 days indicate a larger biomass development on CEMV concretes than on CEMII concretes (greater than 150 a.u). This tendency is confirmed after 360 days of immersion. Furthermore, an increase by 50% of biomass is registered for the CEMV 20%S concrete after 360 days with values increasing from 150 a.u (180 days) to 276 a.u (360 days) (Fig. 5a). The standard deviations are nevertheless relatively high which is explained by the disparity of colonization on the concrete specimens surface.

The results illustrated in Fig. 5b show that the maximum quantum efficiency of PS_{II} (F_v/F_m), which represents the physiological state of the cells, is high (with an average of 0.55) and indicates a very good physiological state. However, the evolution of the F_v/F_m as function of immersing period (180 and 360 days) is not very pronounced for the different concrete mix designs. Thus, the micro-phytobenthos has acclimatized well to the environment conditions and its substrate.

The maximum photosynthetic capacity ($rETR_{max}$) (Fig. 6) of biofilm algal specie varies very slightly between concrete CEMII and CEMV after 180 days with an average of 48.5 μmol.electrons.m^{-2}.s^{-1}. Large differences were noticed in their electron transport activity after 360 days for the biofilm formed on CEMII 20%S concrete. Indeed, CEMII 20%S shows an increased capacity up to 126 μmol.electrons.m^{-2}.s^{-1} (Fig. 6) even if the standard deviation is much larger for this concrete type compared to the other without shells. Therefore, we may suppose that the photosynthetic capacity of the biofilm on CEMII shell concrete varies greatly with the studied area, a behaviour observed in other samples too. Despite these observations, there is no cause and effect of concrete composition on the photosynthetic capacity of microalgae because it depends on the light energy required to saturate photosynthesis. This parameter depends on the species composition of the algal community and their individual photosynthetic capacity. The photosynthetic capacity of microalgae can also be influenced by other abiotic factors such as temperature or nutrient availability. Therefore, it is important to know the species of the biofilm in order to evaluate the primary productivity.

From all these results, it can be concluded that CEMV concrete mixes

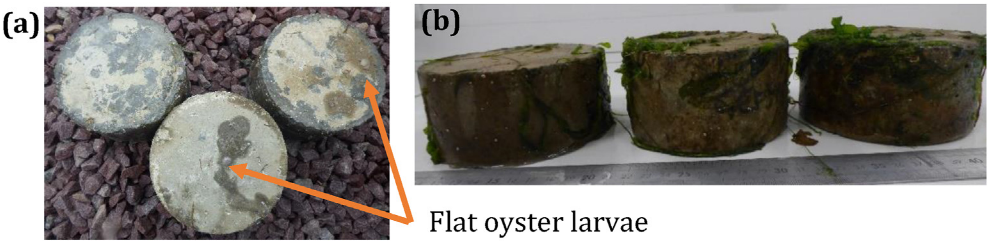


Fig. 4. a): Photograph of CEMII 0% S specimens immersed after 90 days and **b):** after 180 days.

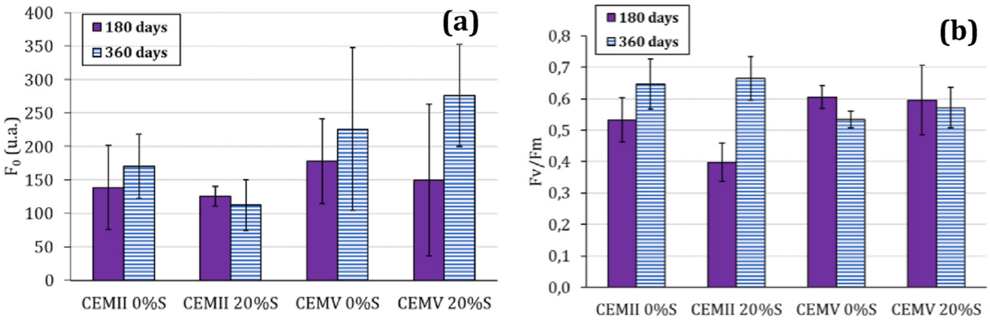


Fig. 5. a): Average of the chlorophyll biomass F_0 index and **b):** Average of the F_v/F_m ratio, for 180 and 360 days of immersion at the surface of concretes.

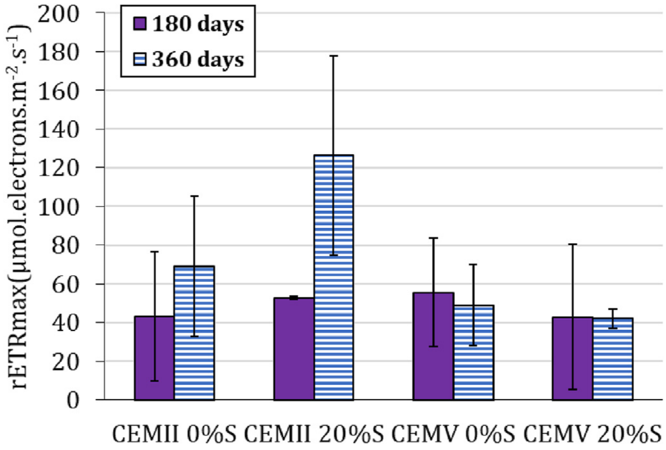


Fig. 6. Average of the Maximum photosynthetic capacity ($rETR_{max}$) of the different concretes immerged after 180 and 360 days.

seems to be more bio-receptive than the CEMII concretes. The colonization kinetics seem to depend more on the type of cement than on the presence of shells in the concrete. Cuadrado et al. (2016b), and Souche et al. (2016), found that the incorporation of shell had no influence on the bio-receptivity of concrete. Moreover, the biofilm activity depends more on extrinsic factors of the surrounding environment than on the substrate composition.

The choice of the best formulation for the conception of new maritime infrastructure thus requires to encompass other factors.

3.2. *Compressive strength*

Mechanical strength mesurements (Fig. 7a) show that the compressive strength obtained after 90 days of curing is significantly larger for the CEMV type concrete (70.53 MPa) compared to that of CEMII (46.3 MPa). A decrease in compressive strengths is noticed when substituting 20% of 4/10 aggregates by shell ones, with values decreasing to 49 MPa and 32 MPa respectively. The decrease in strength for shell-containing concretes is due to several factors. First, the intrinsic stiffness of oyster shells, which are calcitic biocomposites, is lower than those of gravels. Furthermore, oyster shell is caraterised by foliated and prismatic calcite layer microstructure. Second, calcite is strongly mechanically anisotropic. If such microstructures are unproperly oriented within the concrete, they can easily offer weak mechanical resistance by clivage under mechanical stress. This mechanical behaviour can be also affected by the important oyster shell water absorption and the presence of organic impurities (Cuadrado et al., 2016b). In addition, the introduction of shells also increases the total porosity which decreases the concrete mechanical properties.

A compressive strength increase is observed for all concretes after immersion in natural and artificial seawaters compared to the respective reference concretes, except for CEMV without shells (Fig. 7b). Thus, despite a high strength at 90 days of curing, CEMV 0%S is less resistant in the seawater environment compared to other concretes. Furthermore, this mechanical loss increases with time in NSW (Fig. 7a).

The compressive strength increase for the concretes CEMII 0%S, CEMII 20%S and CEMV 20%S, after immersion in salty environment, can be explained by carbonation.

To investigate the carbonation hypothesis, thermogravimetric analysis were carried out. An example of the obtained results (CEMII concretes) is shown in Fig. 8.

It can be noticed that, after immersion, the CEMII concretes exhibit an increase in calcium carbonate (decomposition peak between 600 and 900 °C (Villain et al., 2007). This phase formation is due to the phenomenon of carbonation of the cementitious material. Indeed, the $MgCl_2$, naturally present in seawater, can induce the release of Ca^{2+} from the hydrate $Ca(OH)_2$, to form $CaCO_3$ (Zhu et al., 2012). Bier (1986) demonstrated that carbonation induces a modification of the cementitious materials pore structure. He showed that this modification depends on the cement type. Indeed, a reduction of capillary pore volume is observed when the cement contains high clinker rate. Thus, we can assume that the increase of compressive strength recorded for CEM II concretes is due to carbonation. Indeed, the CEMII cement used in this study is composed of a large quantity of clinker (81.9%). Other studies (Bier, 1986; Song and Kwon, 2007) showed that the precipitation of $CaCO_3$ closes the pores of the concrete which reduces the porosity leading to an enhancement of the mechanical resistance as observed in this study (Fig. 7ab). However, when the cement containes slag,

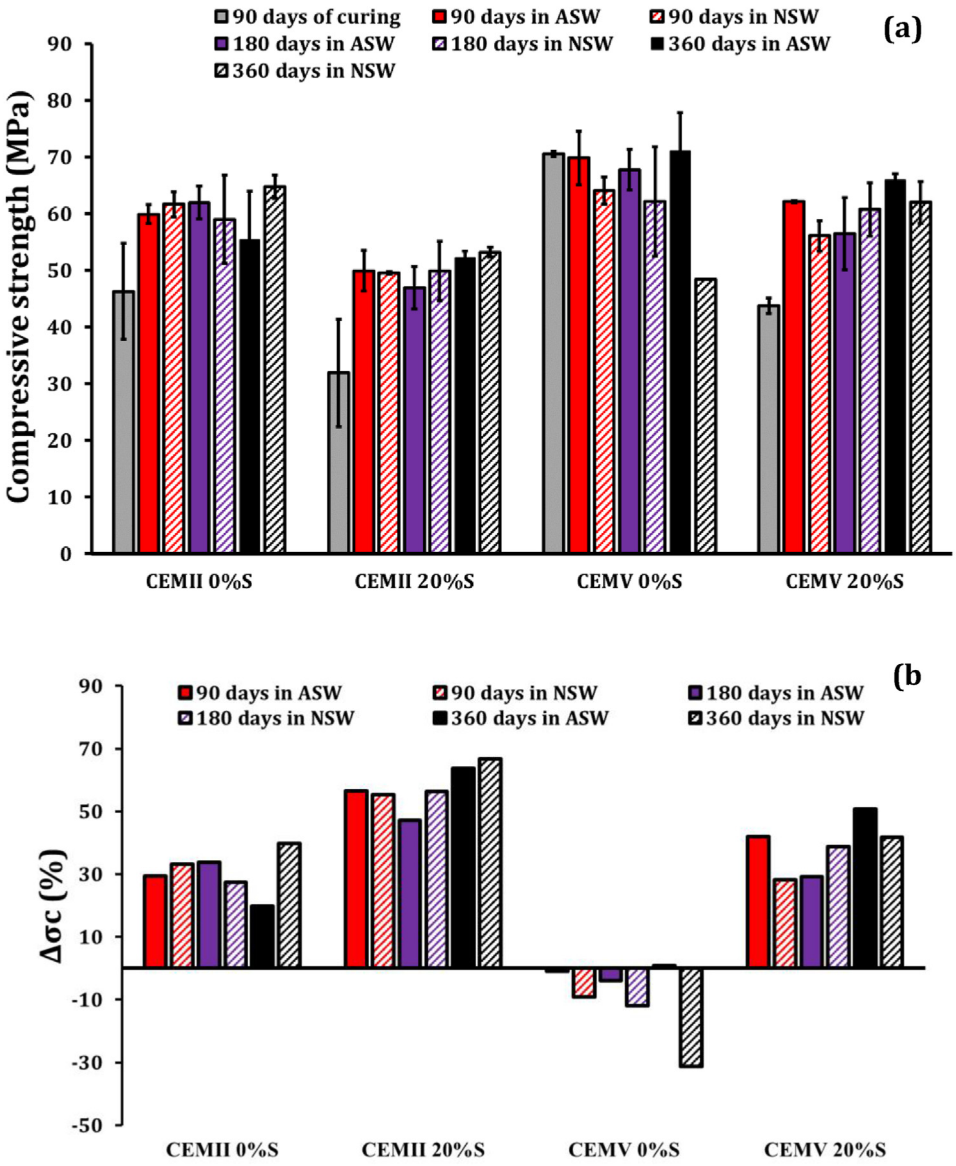
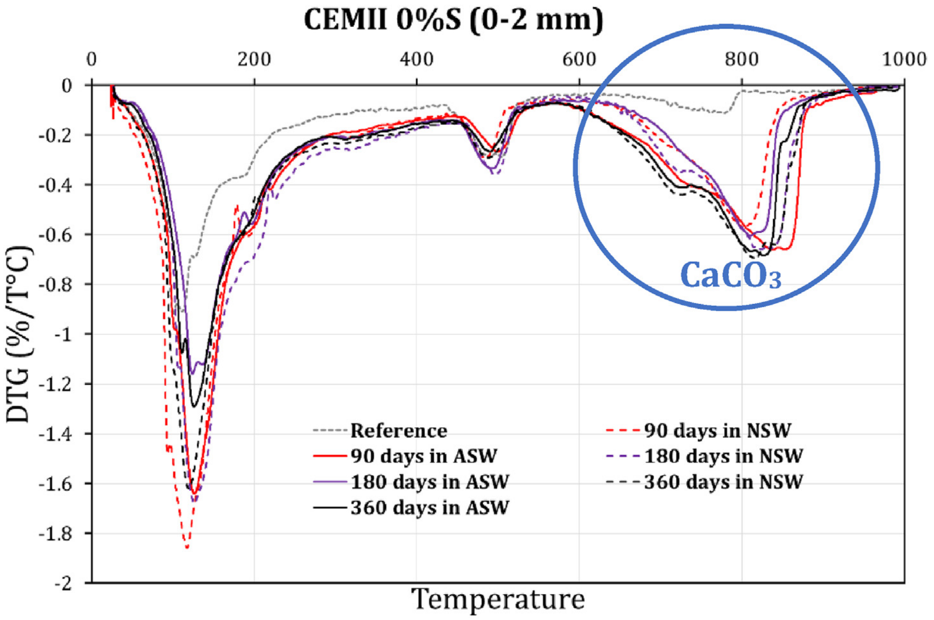


Fig. 7. a): Compressive strength of the concretes after 90 days of curing and after 90, 180 and 360 days immersed in ASW and NSW, and **b):** Relative difference between the respective compressive strengths of immersed and reference concretes.

carbonation generates a coarser capillary pore system. Therefore, the mechanichal strength decrease obtained for the CEM V 0%S concrete (Fig. 7b), can be attributed to carbonation according to Bier study (Bier, 1986). Indeed, the blended cement CEMV used in this study, containes 22% of slag and 22% of fly ash. Once carbonated, the materials manufactured whith this type of cement are subjected to an increase of porosity (Song and Kwon, 2007) resulting in a loss of durability (Morandeau et al., 2014; De Ceukelaire and Van Nieuwenburg, 1993). Furthermore, the compressive strength loss can be explained by the carbonation of C–S–H which is the main phase responsible of mechanical strength (Cahyadi and Uomoto, 1995; Thiery et al., 2007). As previously mentioned, this change in mechanical performance is even more pronounced in natural seawater (Fig. 7a). Fig. 9 shows the concrete specimens after immersion during 360 days. A biofilm as well as the development of macroalgae can be observed on all the materials surfaces. The aggressive biological agents, produced as a result of the micro-organisms and macro-algae metabolism, embrittle the concrete structure (Bastidas-Arteaga et al., 2008; Jayakumar and Saravanane, 2009, 2010). When the cementitious material is characterized by a high porosity, these aggressive elements can penetrate more deeply into its structure. This explains the more pronounced decline of CEMV 0%S concrete mechanical properties when it is bio-colonized.

Concerning the CEMII concretes, the obtained results showed that the increase in mechanical strength was maintained when samples were immersed in natural seawater (NSW) until 180 days. However, after 360 days, for the CEMII 0%S concrete, the bio-colonization improved its mechanical performance. Therefore, bio-colonization associated with carbonation can be considered as beneficial for this concrete. The accumulation and development of marine organisms on the surface of the CEMII 0%S (Fig. 9) may then act as protective, particularly after 360 days of immersion.

The limited and non-homogeneous quantity of oyster larvae attached after 90 days of immersion in the Dinard bay, does not allow to conclude that the growth of these bivalves, which were clearly visible after 180 and 360 days of immersion (Fig. 9), had a real impact on the resistance of the different concretes. Nevertheless, it is important to take into account the fixation of these calcareous colonizers. Indeed, previous studies (Perkol-Finkel and Sella, 2014; Sella and Perkol-Finkel, 2015; Kawabata et al., 2012; Shuying and Xiaoning, 2018) have shown that such colonization could contribute to protect the structure and thus promote the



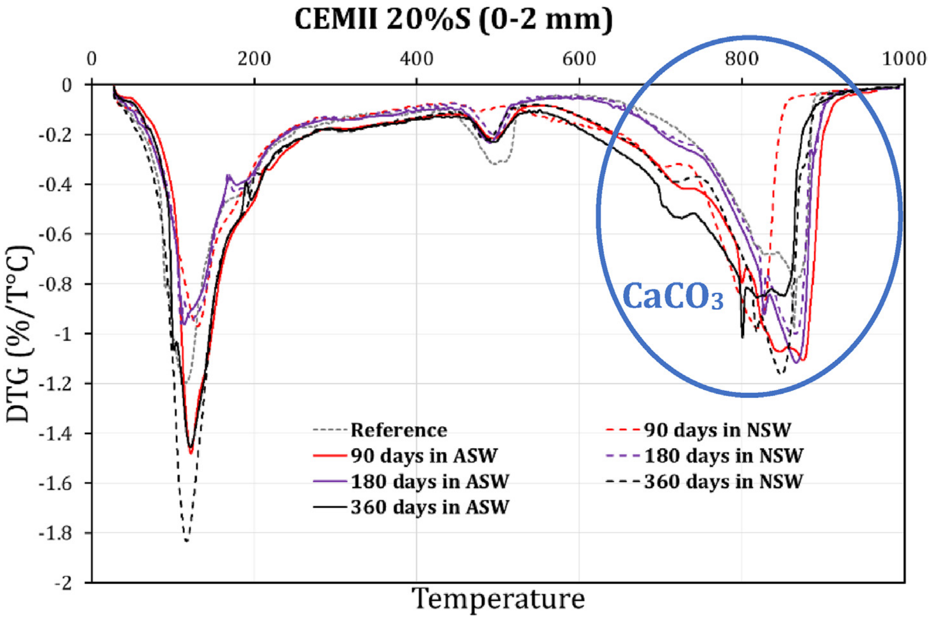


Fig. 8. Thermogravimetric analyses (DTG) of the first milimeters of reference concrete CEMII and immersed in artificial and natural seawater after 90, 180 and 360 days.

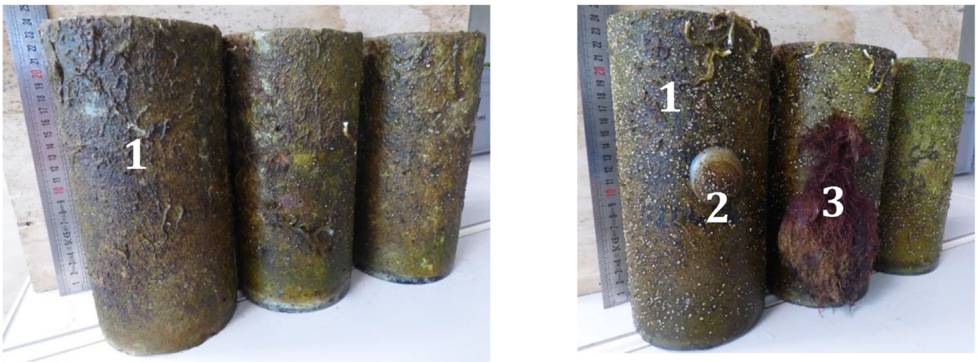
durability of the concrete in the long term. The biogenic growth of oysters can make concrete ten times stronger over the long term compared to concrete without oyster attachment (Risinger, 2012).

We observe (Fig. 7b) an increase of the gain in mechanical strength for both types of concretes containing shells when immersed in marine environment. This mechanical performance enhancement can be explained by a higher carbonation rate than for the other studied concretes which is explained by extra-voids generated by shell aggregates. This phenomenon counter-balanced the registered decrease of the reference concretes mechanical properties when siliceous aggregates were substituted by shell ones thanks to a more dense structure.

3.3. *Chloride ions diffusion tests*

In order to study the durability of the different concretes in the marine environment, chloride ions diffusion tests were carried out. (Fig. 10).

The chloride ions diffusion in CEMII concretes measured in the two environments does not differ between the concretes with and without shells (Fig. 10a and b). An increase of chloride ions concentration is observed in the first millimeters of the materials down to around 6 mm of depth from which it tends to stabilize. In the short terms (90 and 180 days), free Cl-concentrations are overall larger for samples immersed in NSW (dashed lines) at all depths and whatever the shells content in the samples. Therefore, it can be concluded that bio-colonization decreases the durability of theses concretes. However, at 360 days, larger chloride



CEMII 0%S **CEMII 20%S**

CEMV 0%S **CEMV 20%S**

Fig. 9. Colonization of concrete specimens after 360 days in natural seawater on 11 × 22 cm cylindrical samples (1: Biofilm; 2: Flat oyster larvae; 3: Rhodophyta; 4: Chlorophyta; 5: Calcareous tubeworms).

ions content is found in samples immersed in ASW compared to those in NSW. This result significates that bio-colonization have, for long terms, a protective action against chloride ions penetration.

We can notice that, when immersed in artificial seawater for 360 days, the presence of oyster shell aggregates in CEMV concrete enhances chloride ions content by a factor of nearly 2 in the first millimeters compared to concrete without shells (Fig. 10c and d, solid lines). This result can be explained by a higher carbonation rate in CEMV 20%S concrete than that in CEMV 0%S one, when exposed to ASW, which is due to the extra-voids generated by shell aggregates. Indeed, the carbonation reduces the chloride-binding capacity of the cementitious matrix (Balonis et al., 2010; Jakobsen et al., 2016; Zibara, 2001) thus leading to a higher free chloride ions concentration in pore solution in CEMV 20%S concrete than in CEMV 0%S one.

The biomass growth was larger on the surface of the CEMV 20%S sample (Fig. 5a) at 360 days of immersion, which may explain the decrease in the diffusion of chloride ions compared to the CEMV 0%S concrete. Indeed, at 4 mm of depth, the registered value for CEMV 20%S was 2165 mg/kg of concrete while a free Cl-concentration of 2964 mg/kg of concrete was obtained for CEMV 0%S. Moreover, ionic profiles for the specimens immersed in ASW and thus not colonized show an increase of the chloride ions concentration in the cementitious matrix up to 8 mm. These results are also observed after 360 days of immersion of CEMII type concretes (Fig. 9a and b). It can then be hypothesized that the accumulation of biofilm on the long term in natural seawater plays a role of protective barrier against the action of chloride ions, as observed previously by Shuying and Xiaoning (2018).

Other studies have shown that, in the long term, the diffusion of chloride ions is less important when the material is covered by numerous sessile organisms (Chlayon et al., 2020; Chlayon et al., 2018; Coombes et al., 2013; Coombes et al., 2017; La Marca et al., 2015). These results mainly concern concretes immersed in the intertidal zone, which is not the case in our study. Furthermore, Lv et al. (2015), showed that oyster larvae have a protective effect on concrete by limiting the penetration of chloride ions thanks to their secretions. Indeed, they secrete a biological cement (bio-organic calcareous-based adhesive proteins) to attach to the surface of a material (TibabuzoPerdomo et al., 2018). Hence the importance of creating bio-receptive materials for these target species.

The study of concretes durability against chloride ions diffusion leads to an important point: the total chloride ions content in concretes varies more according to the cement type than the presence of shells. Indeed, in the first 6 mm, whatever the used conditions (with and without shells, seawater) the CEMII based concretes are more sustainable than those elaborated with CEMV. For CEMII, chloride ions concentration does not exceed 1500 mg/kg of concrete in the first millimeters in natural seawater (Fig. 10a and b), while in CEMV (Fig. 10c and d) this concentration is at least twice this amount (up to 3300 mg/kg of concrete).

4. Conclusion

This study's main objective was to develop and optimize different concrete mix designs and determine the most sustainable during its

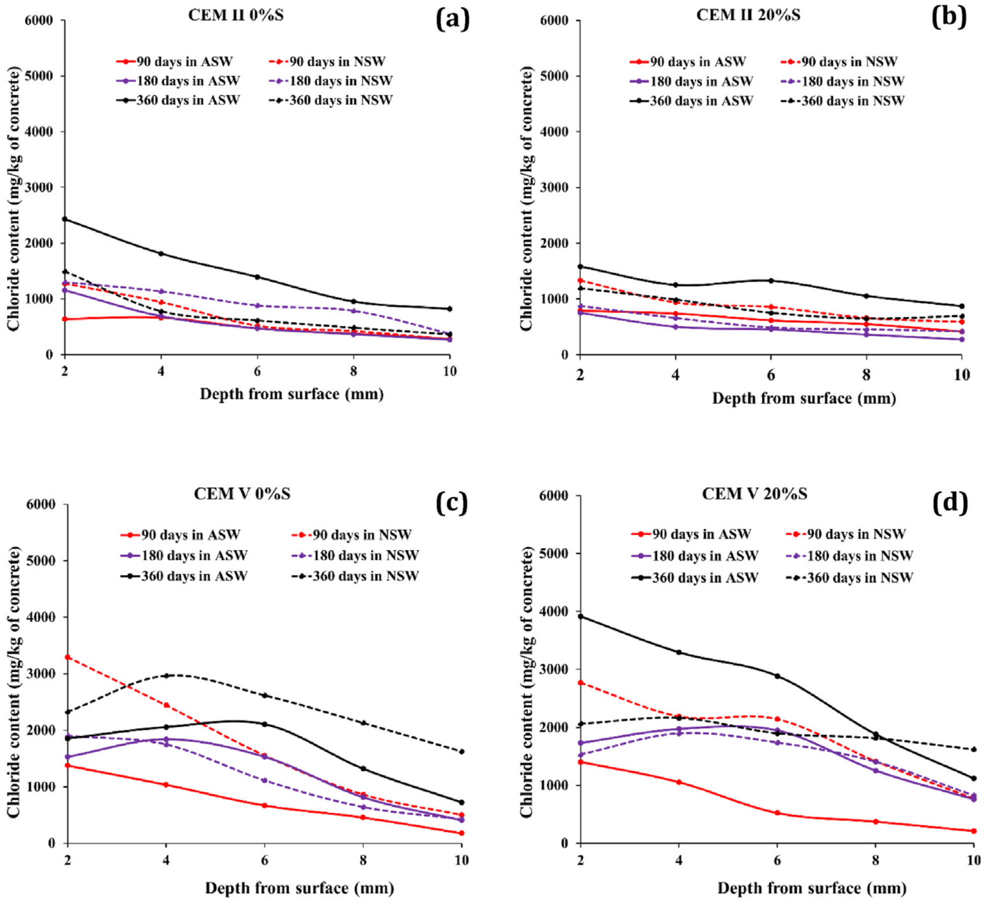


Fig. 10. Chloride ions content up to 10 mm of depth in the samples, against immersion times for Artificial SeaWater (solid line) and Natural SeaWater (dashed line) for the CEMII (**a** and **b**) and CEMV (**c** and **d**) concretes with (**b** and **d)** and without (**a** and **c**) shells.

immersion in a marine natural environment. These findings open the way to a better understanding of the links between the concrete properties both on its microstructure and durability and the effects of its immersion in natural seawater. Variation of the type of cement or the addition of shell aggregates has a significant effect on the durability and strength of these materials.

The monitoring of the photosynthetic activity of biofilms and their biomass on the materials surface showed a better acclimatisation of the microphytobenthos in the substrat CEMII 20%S than in other concretes despite a lower colonization on this concrete. The chlorophyll biomass was higher in concrete CEMV 20%S after 360 days with a total of 276 a.u than the other concretes.

The presence of shells considerably reduces the strength of the material after 90 days of curing. During immersion (ASW or NSW), the mechanical strengths of CEMII 0%S, CEMII 20%S and CEMV 20%S increased. This behaviour can be explained by their carbonation.

With regard to the chloride ions diffusion at long term, Cl^- ions content was reduced in concrete CEMII 0%S, CEMII 20%S and CEMV 20%S when they were immersed in natural seawater. We can conclude that bio-colonization protects the concrete against chloride ions aggression. Moreover, biotic and abiotic factors are different depending on the immersion zone and have a major impact on the material. The impact of organisms on durability of concrete could depend on the organism type attached on the specimen surface. This study also highlighted that the chloride ions diffusion seems to depend more on the cement type than on the quantity of shells.

Finally, it appeared from this study that the concrete CEMII 20%S is the most suitable concrete mix design for the marine infrastructure manufacturing especially if they should contain frames.

This study reveals also the importance of small-scale testing and long-term monitoring before the conception of marine infrastructures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Ammar, Y., Swailes, D., Bridgens, B., Chen, J., 2015. Influence of surface roughness on the initial formation of biofilm. Surf. Coating. Technol. 284, 410–416. https://doi:10.1016/j.surfcoat.2015.07.062.

Atkinson, M., Bingma, C., 1997. Elemental composition of commercial seasalts. J. Aquaric. Aquat. Sci. VIII 2, 39–43.

Balonis, M., Lothenbach, B., Le Saout, G., Glasser, F.P., 2010. Impact of chloride on the mineralogy of hydrated Portland cement systems. Cement Concr. Res. 40, 1009–1022. https://doi.org/10.1016/j.cemconres.2010.03.002.

Bastidas-Arteaga, E., Sánchez-Silva, M., Chateauneuf, A., Silva, M.R., 2008. Coupled reliability model of biodeterioration, chloride ingress and cracking for reinforced concrete structures. Struct. Saf. 30, 110–129. https://doi.org/10.1016/j.strusafe.2006.09.001.

Bergen, S.D., Bolton, S.M., Fridley, J.L., 2001. Design principles for ecological engineering. Ecol. Eng. 18, 201–210. https://doi:10.1016/S0925-8574(01)00078-7.

Bier, T.H.A., 1986. Influence of type of cement and curing on carbonation progress and pore structure of hydrated cement pastes. MRS Online Proc. Libr. 85 (1), 123. In: https://doi:%2010.1557/PROC-85-123.

Cahyadi, J.H., Uomoto, T., 1995. Relation between phase composition, pore structure and compressive strength of carbonated mortar. J. Mater. Concr. Struct. Pavements. 526, 133–141. https://doi.org/10.2208/JSCEJ.1995.526_133.

Chlayon, T., Iwanami, M., Chijiwa, N., 2018. Combined protective action of barnacles and biofilm on concrete surface in intertidal areas. Construct. Build. Mater. 179, 477–487. https://doi.org/10.1016/j.conbuildmat.2018.05.223.

Chlayon, T., Iwanami, M., Chijiwa, N., 2020. Impacts from concrete microstructure and surface on the settlement of sessile organisms affecting chloride attack. Construct. Build. Mater. 239, 117863. https://doi.org/10.1016/j.conbuildmat.2019.117863.

Coombes, M.A., Naylor, L.A., Viles, H.A., Thompson, R.C., 2013. Bioprotection and disturbance: seaweed, microclimatic stability and conditions for mechanical weathering in the intertidal zone. Geomorphology 202, 4–14. https://doi.org/10.1016/j.geomorph.2012.09.014.

Coombes, M.A., La Marca, E.C., Naylor, L.A., Thompson, R.C., 2015. Getting into the groove: opportunities to enhance the ecological value of hard coastal infrastructure using fine-scale surface textures. Ecol. Eng. 77, 314–323. https://doi:10.1016/j.ecoleng.2015.01.032.

Coombes, M.A., Viles, H.A., Naylor, L.A., La Marca, E.C., 2017. Cool barnacles: do common biogenic structures enhance or retard rates of deterioration of intertidal rocks and concrete? Sci. Total Environ. 580, 1034–1045. https://doi.org/10.1016/j.scitotenv.2016.12.058.

Cuadrado, H.R., Boutouil, M., Boudart, B., Claquin, P., Leroy, F., 2016b. Colonisation et détérioration des bétons incorporant des coquilles pour récifs artificiels. Mater. Technol. 104, 503. https://doi.org/10.1051/mattech/2017005.

Cuadrado, H.R, Sebaibi, N., Boutouil, M., Boudart, B., 2016a. Properties of ordinary concretes incorporating crushed queen scallop shells. Mater. Struct. 49, 1805–1816. https://doi.org/10.1617/s11527-015-0613-7.

Cwalina, B., 2008. Biodeterioration of concrete. Archit. Civ. Eng. Environ. 1, 133–140.

De Ceukelaire, L., Van Nieuwenburg, D., 1993. Accelerated carbonation of a blast-furnace cement concrete. Cement Concr. Res. 23 2, 442–452. https://doi:10.1016/0008-8846(93)90109-M.

De Muynck, W., Ramirez, A.M., De Belie, N., Verstraete, W., 2009. Evaluation of strategies to prevent algal fouling on white architectural and cellular concrete. Int. Biodeterior. Biodegrad. 63, 679–689. https://doi:10.1016/j.ibiod.2009.04.007.

Dennis, H.D., Evans, A.J., Banner, A.J., Moore, P.J., 2018. Reefcrete: reducing the environmental footprint of concretes for eco-engineering marine structures. Ecol. Eng. 120, 668–678. https://doi:10.1016/j.ecoleng.2017.05.031.

Eziefula, U.G., Ezeh, J.C., Eziefula, B.I., 2018. Properties of seashell aggregate concrete: a review. Construct. Build. Mater. 192, 287–300. https://doi.org/10.1016/j.conbuildmat.2018.10.096.

Firth, L.B., Mieszkowska, N., Thompson, R.C., Hawkins, S.J., 2013. Climate change and adaptational impacts in coastal systems: the case of sea defences. Environ. Sci. Process. Impacts 15, 1665–1670. https://doi:10.1039/C3EM00313B.

Firth, L.B., Thompson, R.C., Bohn, K., Abbiati, M., Airoldi, L., Bouma, T.J., Bozzeda, F., Ceccherelli, V.U., Colangelo, M.A., Evans, A., et al., 2014. Between a rock and a hard place: environmental and engineering considerations when designing coastal defence structures. Coast. Eng. 87, 122–135. https://doi:10.1016/j.coastaleng.2013.10.015.

Firth, L.B., Browne, K.A., Knights, A.M., Hawkins, S.J., Nash, R., 2016. Eco-engineered rock pools: a concrete solution to biodiversity loss and urban sprawl in the marine environment. Environ. Res. Lett. 11, 094015. https://doi:10.1088/1748-9326/11/9/094015.

Gallon, R.K., Ysnel, F., Feunteun, E., 2013. Optimization of an "in situ" subtidal rocky-shore sampling strategy for monitoring purposes. Mar. Pollut. Bull. 74, 253–263. https://doi.org/10.1016/j.marpolbul.2013.06.049.

Genty, B., Briantais, J.M., Baker, N.R., 1989. The relationship between the quantum yield of photosynthetic electron transport and quenching of chlorophyll fluorescence. Biochim Biophys Acta BBA - Gen Subj. 990 (1), 87–92. https://doi.org/10.1016/S0304-4165(89)80016-9.

Glasby, T.M., 2000. Surface composition and orientation interact to affect subtidal epibiota. J. Exp. Mar. Biol. Ecol. 248, 177–190. https://doi:10.1016/S0022-0981(00)00169-6.

Graham, P.M., Palmer, T.A., Pollack, J.B., 2017. Oyster reef restoration: substrate suitability may depend on specific restoration goals. Restor. Ecol. 25, 459–470. https://doi.org/10.1111/rec.12449.

Guillitte, O., 1995. Bioreceptivity: a new concept for building ecology studies. Sci. Total Environ. 167, 215–220, 1995. https://doi:10.1016/0048-9697(95)04582-L.

Hanlon, N., Firth, L.B., Knights, A.M., 2018. Time-dependent effects of orientation, heterogeneity and composition determines benthic biological community recruitment patterns on subtidal artificial structures. Ecol. Eng. 122, 219–228. https://doi:10.1016/j.ecoleng.2018.08.013.

Jakobsen, U.H., De Weerdt, K., Geiker, M.R., 2016. Elemental zonation in marine concrete. Cement Concr. Res. 85, 12–27. https://doi.org/10.1016/j.cemconres.2016.02.006.

Jayakumar, S., Saravanane, R., 2009. Biodeterioration of coastal concrete structures by macro algae - chaetomorpha antenninale. Mater. Res.-Ibero-Am. J. Mater. - MATER RES-IBERO-AM J MATER 12. https://doi.org/10.1590/S1516-14392009000400015.

Jayakumar, S., Saravanane, R., 2010. Biodeterioration of coastal concrete structures by marine green algae. Int. J. Civ. Eng. 8, 352–361.

Jones, C.G., Lawton, J.H., Shachak, M., 1994. Organisms as ecosystem engineers. Oikos 69, 373–386. https://doi:10.2307/3545850.

Juneau, P., Green, B.R., Harrison, P.J., 2005. Simulation of Pulse-Amplitude-Modulated (PAM) fluorescence: limitations of some PAM-parameters in studying environmental stress effects. Photosynthetica 43, 75–83. https://doi.org/10.1007/s11099-005-5083-7.

Kawabata, Y., Kato, E., Iwanami, M., 2012. Enhanced long-term resistance of concrete with marine sessile organisms to chloride ion penetration. J. Adv. Concr. Technol. 10, 151–159. https://doi.org/10.3151/jact.10.151.

La Marca, E.C, Coombes, M., Viles, H.A., Naylor, L.A., 2015. The bio-protective role of a biological encrustation. Biol. Mar. Mediterr. 21 (1), 345–346.

Lv, J., Mao, J., Ba, H., 2015. Influence of Crassostrea gigas on the permeability and microstructure of the surface layer of concrete exposed to the tidal zone of the Yellow Sea. Biofouling 31, 61–70. https://doi.org/10.1080/08927014.2014.999235.

Ly, O., Yoris-Nobile, A.I., Sebaibi, N., Blanco-Fernandez, E., Boutouil, M., Castro-Fresno, D., Hall, A.E., Herbert, R.J.H., Deboucha, W., Reis, B., et al., 2020. Optimisation of 3D printed concrete for artificial reefs: biofouling and mechanical analysis. Construct. Build. Mater. 121649. https://doi:10.1016/j.conbuildmat.2020.121649.

Manso, S., Calvo-Torras, M.Á., De Belie, N., Segura, I., Aguado, A., 2015. Evaluation of natural colonisation of cementitious materials: effect of bioreceptivity and environmental conditions. Sci. Total Environ. 512–513, 444–453. https://doi:10.1016/j.scitotenv.2015.01.086.

Mehta, P.K., 2019. Concrete in the Marine Environment, 1st. Taylor & Francis.

Morandeau, A., Thiéry, M., Dangla, P., 2014. Investigation of the carbonation mechanism of CH and C-S-H in terms of kinetics, microstructure changes and moisture properties. Cement Concr. Res. 56, 153–170. https://doi.org/10.1016/j.cemconres.2013.11.015.

Nf En 1097-6, January 2014. Tests for Mechanical and Physical Properties of Aggregates —Part 6: Determination of Particle Density and Water Absorption.

Nf En 12350-2, June 2019. Testing Fresh Concrete — Part 2: Slump Test.

Nf En 12350-7, June 2019. Testing Fresh Concrete - Part 7: Air Content - Pressure Methods.

Nf En 12390-3, June 2019. Testing Hardened Concrete - Part 3: Compressive Strength of Test Specimens.

Nf En 206+A1, November 2016. Concrete - Specification, Performance, Production and Conformity.

Nf En 932-2, August 1999. Tests for General Properties of Aggregates — Part 2: Methods for Reducing Laboratory Samples.

Perkol-Finkel, S., Sella, I., 2014. Ecologically active concrete for coastal and marine infrastructure: innovative matrices and designs. In: From Sea to Shore ? Meeting the Challenges of the Sea. ICE Publishing, pp. 1139–1149.

Pioch, S., Relini, G., Souche, J.C., Stive, M.J.F., De Monbrison, D., Nassif, S., Simard, F., Allemand, D., Saussol, P., Spieler, R., et al., 2018. Enhancing eco-engineering of coastal infrastructure with eco-design: moving from mitigation to integration. Ecol. Eng. 120, 574–584. https://doi:10.1016/j.ecoleng.2018.05.034.

Risinger, J., 2012. Biologically Dominated Engineered Coastal Breakwaters. LSU Dr. Diss [Online]. https://digitalcommons.lsu.edu/gradschool_dissertations/3300.

Sanchez-Silva, M., Rosowsky, D.V., 2008. Biodeterioration of construction materials: state of the art and future challenges. J. Mater. Civ. Eng. 20, 352–365. https://doi.org/10.1061/(ASCE)0899-1561(2008)20:5(352).

Sella, I., Perkol-Finkel, S., 2015. Blue is the new green – ecological enhancement of concrete based coastal and marine infrastructure. Ecol. Eng. 84, 260–272. https://doi:10.1016/j.ecoleng.2015.09.016.

Shuying, G., Xiaoning, T., 2018. Impact mechanism of marine biofilm on concrete durability. Chem. Eng. Trans. 64, 613–618. https://doi.org/10.3303/CET1864103.

Song, H.W., Kwon, S.J., 2007. Permeability characteristics of carbonated concrete considering capillary pore structure. Cement Concr. Res. 37 6, 909–915. https://doi:10.1016/j.cemconres.2007.03.011.

Souche, J.C., Saout, G.L., Salgues, M., Pioch, S., 2016. Effets de bétons bio-actifs sur la colonisation marine en environnement méditerranéen. Mater. Technol. 104, 504. https://doi.org/10.1051/mattech/2016033.

Strain, E.M.A., Olabarria, C., Mayer-Pinto, M., Cumbo, V., Morris, R.L., Bugnot, A.B., Dafforn, K.A., Heery, E., Firth, L.B., Brooks, P.R., et al., 2018. Eco-engineering urban infrastructure for marine and coastal biodiversity: which interventions have the greatest ecological benefit? J. Appl. Ecol. 55, 426–441. https://doi:10.1111/1365-2664.12961.

Thiery, M., Villain, G., Dangla, P., Platret, G., 2007. Investigation of the carbonation front shape on cementitious materials: effects of the chemical kinetics. Cement Concr. Res. 37 (7), 1047–1058. https://doi:%2010.1016/j.cemconres.2007.04.002.

Tibabuzo Perdomo, A.M., Alberts, E.M., Taylor, S.D., Sherman, D.M., Huang, C.P., Wilker, J.J., 2018. Changes in cementation of reef building oysters transitioning from larvae to adults. ACS Appl. Mater. Interfaces 10, 14248–14253. https://doi.org/10.1021/acsami.8b01305.

Villain, G, Thiery, M, Platret, G, 2007. Measurement methods of carbonation profiles in concrete: Thermogravimetry, chemical analysis and gammadensimetry. Cem. Concr. Res. 37, 1182–1192. https://doi.org/10.1016/j.cemconres.2007.04.015.

Vivier, B., Dauvin, J.C., Navon, M., Rusig, A.M., Mussio, I., Orvain, F., Boutouil, M., Claquin, P., 2021. Marine artificial reefs, a meta-analysis of their design, objectives and effectiveness. Global Ecology and Conservation 27, e01538. https://doi.org/10.1016/j.gecco.2021.e01538.

Webb, W.L., Newton, M., Starr, D., 1974. Carbon dioxide exchange of Alnus rubra. Oecologia 17, 281–291. https://doi.org/10.1007/BF00345747.

Yi, Y., Zhu, D., Guo, S., Zhang, Z., Shi, C., 2020. A review on the deterioration and approaches to enhance the durability of concrete in the marine environment. Cement Concr. Compos. 113, 103695. https://doi.org/10.1016/j.cemconcomp.2020.103695.

Zhu, Q., Jiang, L., Chen, Y., Xu, J., Mo, L., 2012. Effect of chloride salt type on chloride binding behavior of concrete. Construct. Build. Mater. 37, 512–517. https://doi.org/10.1016/j.conbuildmat.2012.07.079.

Zibara, H., 2001. Binding of External Chlorides by Cement Pastes. University of Toronto, National Library of Canada, Department of Civil Engineering.