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Concrete Durability Probed Using Compressive Strength, Chloride Penetration and Porosity Measurements on CEMII and CEMV Concretes Incorporating Mollusc Shell Spares in Artificial and Natural Seawaters

Marine D. Georges[1], Amel. Bourguiba[1], Nassim. Sebaibi[1], Daniel. Chateigner[2] and Mohamed. Boutouil[1]

[1]COMUE Normandie Université, Laboratoire ESITC - ESITC Caen, rue Pierre et Marie Curie 1, 14610 Epron, France, marine.georges@esitc-caen.fr

[2] Normandie Université, CRISMAT UMR CNRS n°6508, ENSICAEN, Université de Caen Normandie, 6 boulevard Maréchal Juin, 14050 Caen, France, daniel.chateigner@ensicaen.fr

Abstract. *The purpose of this study is to improve the recruitment of flat oyster larvae, an endangered species, by means of a specific marine infrastructure made of concrete. This work aims to develop and optimize concrete formulations by varying the type of cement and introducing shellfish by-products into their composition and determine which concrete formulation is the most sustainable to marine organism colonization. Indeed, it is essential to obtain a sustainable concrete submitted to aggressive marine environment (chloride ions diffusion and bio-colonisation). Four concrete formulations were tested with two types of cements (CEMII and CEMV) and with or without the incorporation of shell aggregates. The durability of these materials was tested after 3 months of immersion in the Rance of Dinard (France). It appears from this study that the CEMII concrete exhibits a good mechanical resistance independently of the presence of shell, after immersion in situ. This concrete also shows better resistance to chloride ions diffusion than CEMV. However, CEMV possess larger compressive strengths than CEMII, and mollusc shells incorporation does not decrease this strength as much as for CEMII. Shell incorporation in the concretes has an effect on strength, chloride penetration and porosity which depend on the used cement and seawater.*

Keywords: *Flat Oyster Larvae, Marine Infrastructure, Concrete, Bio-Colonisation, Durability.*

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 the residual impacts by generating an equivalent gain in biodiversity.

This study is carried out within the framework of the European Marineff project, which is part of this context. One of this study‘s objectives is the design of maritime infrastructures for flat oysters (*Ostrea edulis* Linnaeus, 1758) restoration in the Channel. Indeed, the flat oyster is an endangered species.

Over the years, a new approach has emerged, in the aim of enhancing marine infrastructure (surface condition, structure and composition) to promote ecological succession (Firth *et al*., 2014; Perkol-Finkel and Sella, 2014; Sella and Perkol-Finkel, 2015). Thus, the term "ecological engineering" emerged (Bergen *et al*., 2001; Dennis *et al*., 2018; Firth *et al*., 2014, 2016; Pioch *et al*., 2018; Strain *et al*., 2018). The 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 (Coombes *et al*., 2015; Hanlon *et al*., 2018; Jones *et al*., 1994).

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, physical and biological attacks that can lead to its deterioration (Bastidas-Arteaga *et al*., 2008; 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.

Using a combination of laboratory and field experiments, we aimed to: (1) develop and optimize concrete formulations by varying the type of cement and introducing shellfish by-products into their composition (2) determine which concrete formulation is the most sustainable following the colonization of marine organism.

2 Material and Methods

2.1 Concrete's Formulations

For this study, 4 concrete formulations were designed with 2 types of cement, Portland cement (Calcia), CEM II/A-LL 42.5 R CE PM-CP2 NF and CEM V/A (S-V) 32.5 N-LH CE PM-ES-CP1 NF. These two types of cement are suitable for use in sea waters. Siliceous alluvial sand was used in granular class 0/2. Alluvial aggregates were also used and are composed of two sizes, 4/10 and 10/20 (Figure 1). A substitution of 20% of the aggregates (D4/10) by oyster shell aggregates was made to study the effect of this biomineral by-product on the recruitment of oyster larvae. Indeed, the incorporation of mollusc shell aggregates can increase the bio-receptivity of concrete because they provide an ideal substrate for the settlement of marine organisms (Graham *et al*., 2017; Hanlon *et al*., 2018).

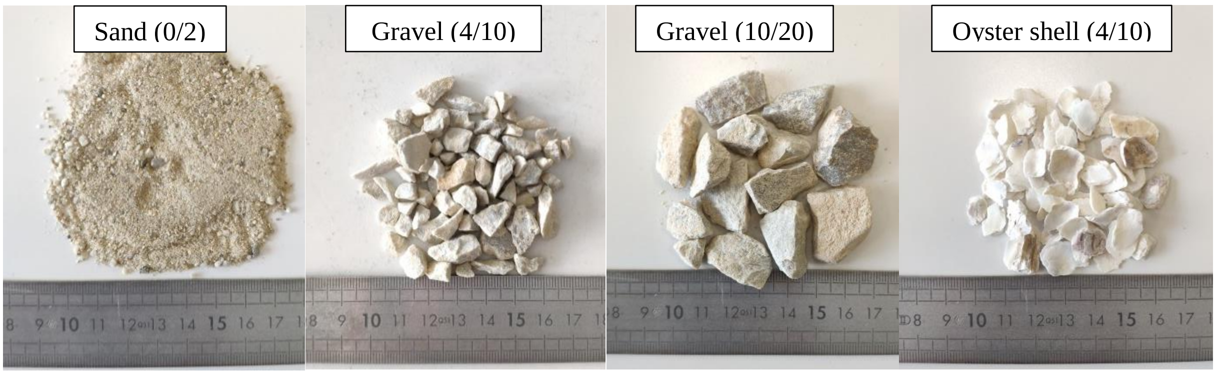


Figure 1. The various types of aggregates used to elaborate the concretes of this study.

After the characterization of the raw materials, concrete mix designs formulation was carried out in accordance with EN 206-1. The four studied concrete formulations are given in Table 1.

Table 1. Concrete's formulations (Proportions given in kg/m^3 of concrete).

Formulations / Components	F1 : CEM II without shell	F2 : CEM II with 20 % shell	F3 : CEM V without shell	F4 : CEM V with 20 % shell
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	-	121	-	121
Water	175	175	175	169
Superplastifiant	1.28 %	2%	1.28 %	2%

2.2 Concrete Durability Against Marine Environment

To study the sustainability of the concretes in marine environment, 11-cm diameter cylindrical samples with heights of either 22 cm or 5 cm were elaborated. Before their immersion in the Rance river of Dinard (France), the samples were placed in cages (iron grids). The immersion was carried out during 3 months to study marine organisms colonisation on the samples. After this period, mechanical and durability tests were carried out.

2.2.1 Compression test

The compression tests were carried out on the 11 cm × 22 cm cylindrical samples using a 3R press (4000 kN) after 90 days of curing (reference concrete) and after 90 days immersed in natural seawater. The test was operated in accordance within the NF EN 12390-3 standard.

2.2.2 Chloride ion diffusion tests

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 powder produced by drilling was collected, filtered and diluted to 1/25th before being analyzed by a 883 Basic IC Ion Chromatograph using standard preparation procedures. The obtained leachate is also used to measure the pH of the material. This test was carried out on the samples immersed natural seawater and in artificial seawater.

2.2.3 Porosity accessible to water

Porosity is an important factor that influences the material's durability. This test was carried out on the immersed samples (natural seawater*)* and after 90 days of curing (reference concrete), according to the NF P18-459 standard.

The value of the porosity (p) is obtained by the equation (1):

$$\mathrm{p} = \frac{M_{sds} - M_d}{M_{sds} - M_w} \times 100 \tag{1}$$

Where M_{sds} is the saturated dry surfaces sample mass, M_d the dry sample mass and M_w the mass in water.

3 Results and Discussion

In order to choose the best concrete formulation, several mechanical strength and durability tests were carried out. The 11x22 samples were colonised by sessile fauna and some macro-algae after 3 months of immersion in natural seawater. We could count some bryozoans, sponges, serpulid and spiral tubes of Spirorbs (Figure 2).

Figure 2. Concrete samples (11x22) after immersion for 3 months in natural seawater.

3.1 Compression Test

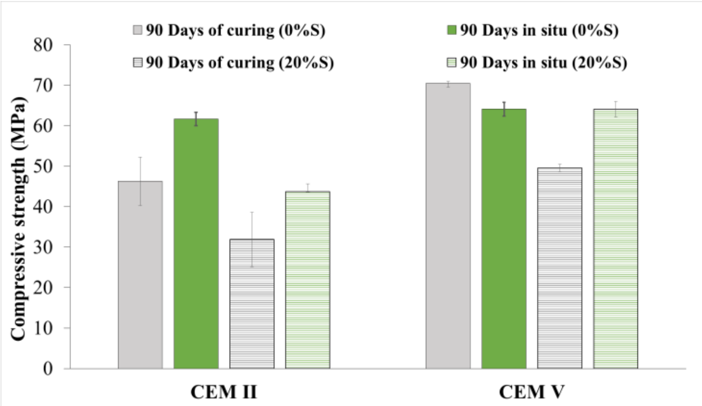
Mechanical strength results (Figure 3) show that, without shell incorporation, the compressive strength obtained after 90 days of curing is significantly higher for the CEMV type concrete (70.53 MPa) compared to CEMII (46.3 MPa) (Figure 3, A). A decrease in compressive strengths is noticed when adding shell aggregates, with values decreasing to 49 MPa and 32 MPa respectively. The compressive strength increases for all concretes except for CEMV without shells after 3 months of immersion in natural seawater compared to the reference concrete. This increase is larger for concretes containing shell aggregates, with approximately 35% larger strengths for CEMII with shells and 24% without (Figure 3, B). Interestingly, in CEMV concretes this latter tendancy is even increased, immersion in seawater inducing a decrease of compressive strength after 3 months without shell incorporations, while addition of shells increases the compressive response inside seawater. CEMV even exhibits the same compressive strength after 3 months of immersion with or without shells.

Rica *et al.*, 2016 also studied the effect of colonisation on the mechanical strengths of several cementitious materials with and without shells at different timescales *in situ*. It was found that self-placing concrete with 40% of shells showed an increase in resistance (+8%) after an immersion of 22 weeks in seawater compared to 28 days of curing in the laboratory.

Shells are natural biominerals that do not modify intrinsically after immersion in seawater, even for long times after death. Consequently, if shell-cement interfaces are enough bounding them together, the resulting mechanical strength variations of the concrete over time are assumed to depend more on the cement behaviour. In our experiments bonding properties are not probed, but even after 90 days of curing, the cementing part of the concretes are not fully matured and are potentially subjected to suffer some alteration in the aggressive seawater medium. This is at least the case for CEMV which exhibits a clear decrease in compressive strength after 3 months of immersion, and contraily to CEMII. But in shell-containing concretes compressive strength increase is observed for the two types of concretes. The effect of shell incorporation cannot be a simple steric effect with less deterioration thanks to shell additions, since this would only reduce the compressive strength decrease of CEMV comparing with and without shell.

We are then concluding that another effect occurs, beneficial to and not only buffering strength decrease. The mechanism for such an effect is not monitored by our experiments, and further investigations are needed to explain our results. A modification of the concrete microstructure due to calcium carbonates and organic species contained in the shells could be at the origin of the observed behaviour.

A)



B)

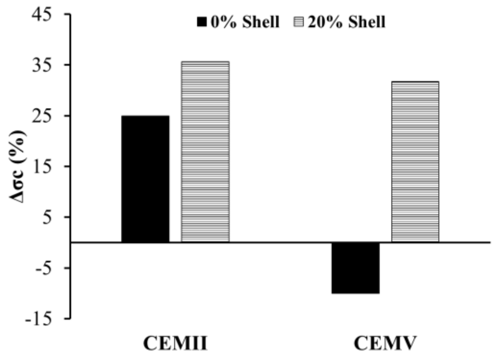


Figure 3. (A): Compressive strength of the different concrete formulations after 90 days of curing and after 90 days in natural seawater; (B) : Difference between the resistance of concretes immersed in seawater for 90 days vs. cured at 100% RH (90 days).

3.2 Chloride Ion Diffusion Tests

The durability of concrete mix designs against chloride ions diffusion were then studied after immersion in two different environments: artificial and natural seawaters. The evolution of the chloride ions content (as a function of depth and environment) is represented in Figure 4. We can also notice that after 3 months of immersion in natural seawater, we obtain higher chloride ions content between 0 and 6 mm for the concrete mix designs manufactured without shells compared to those immersed in artificial seawater (Figure 4 A and C). This result can be explained by the fact that the bio-colonisation of samples facilitates the penetration of Cl^- ions.

In artificial seawater (ASW, Figure 4, solid lines), the presence of shells in the concrete (Figure 4B and D) tends to enhance chloride content by a factor of nearly 2 in the first millimeters compared to concretes without shells (Figure 4A and C). This tendancy is not observed for immersions in natural seawaters (NSW, dotted lines). The reason for such a behaviour could be seen in partial dissolution of shell pieces, which is more pronounced in artificial seawaters. Part of the molecules and macromolecules contained in shells are Water Soluble (WSM), and present in NSW but not in ASW. Consequently, immersing shells in ASW gives rise to larger chemical potentials than in NSW, tending to operate more dissolution and element infiltrations, the process being or not mediated by chloride ions.

The total chloride content in our concretes varies according to the cement type. In the first six millimetres, whatever the used conditions (with and without shells, seawater) the concretes made with CEMII are more sustainable from the point of view of chlorine penetration than those elaborated with CEMV. For CEMII, chloride content does not exceed 1500 ppm in the first millimetres (Figures 4A and B), while in CEMV (Figure 4C and D) this concentration is at least twice this amount (up to 3700 ppm).

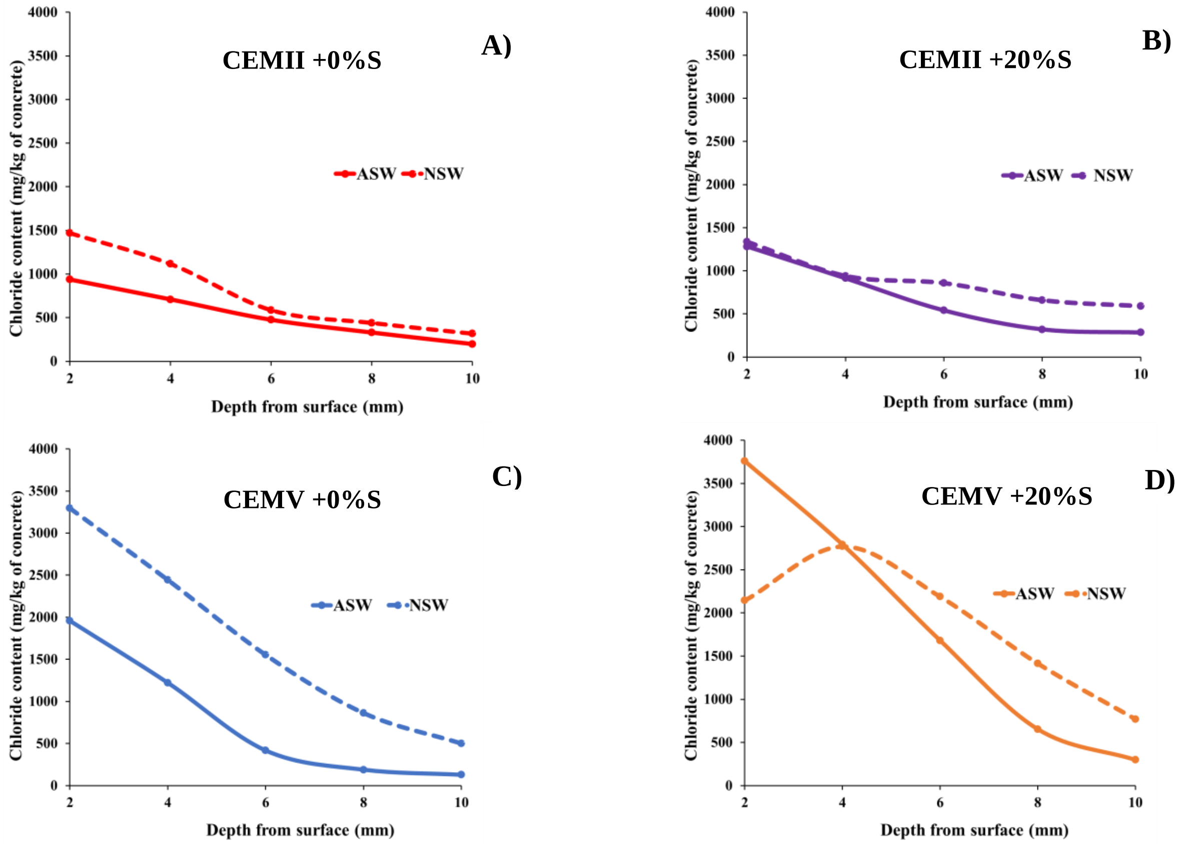


Figure 4. Chloride ions content after an immersion of 1 month in Artificial SeaWater (ASW) (solid line) and after 3 months in Natural SeaWater (NSW) (dotted line) for two different concrete composition CEMII and CEMV without Shells (S) (Respectively A et C) and CEMII and CEMV with Shells (Respectively B et D).

3.3 Porosity Accessible to Water

Measurements of porosity accessible to water (Figure 5) indicate that, except for a slight increase in porosity of around 0.1-0.2%, the two concrete formulations made with CEMII remain stable after immersion for 3 months in natural seawater. This is not the case for CEMV concretes for which we observe a decrease of porosity up to 4% after 3 months. The shell-containing CEMV concrete however exhibit less porosity decrease compared to such a concrete without shells. Such porosity decrease contributes undoubtfully to the compressive strength increase of the CEMV sample with shells.

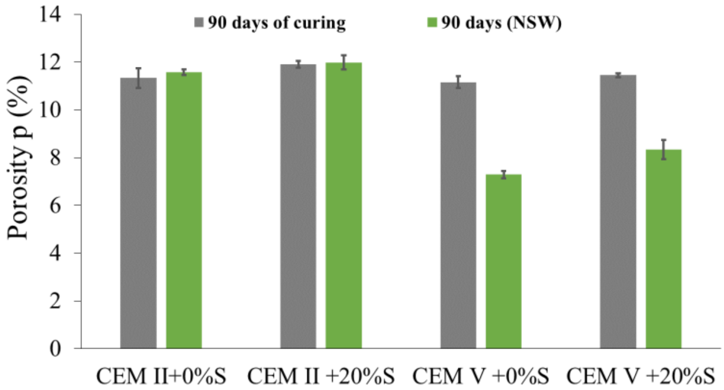


Figure 5. Porosity accessible to water after 90 days of curing and immersed after 90 days in NSW.

4 Conclusion

Our results indicate that the CEMII concrete formulations are the more resilient to chloride penetration in artificial and natural seawaters than CEMV concretes. The incorporation of shell aggregates does not significantly modify chloride penetration in natural seawater but increases it in artificial seawater. Porosities significantly decrease in CEMV concretes after 3 months of immersion, which partly explains the compressive strength increase of this material, while only slight porosity variations are observed in CEMII with aging in seawater. Calcium carbonates partial dissolution is more pronounced in artificial sea water, and combined with an increased chloride ion penetration inside the first millimeters of the materials. Longer term tests of durability are on-going (6 and 12 months), together with monitoring of colonisation by studying photosynthetic parameters.

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ORCID

Nassim Sebaibi: http://orcid.org/0000-0002-1241-2745
Daniel Chateigner: http://orcid.org/0000-0001-7792-8702
Mohamed Boutouil: http://orcid.org/0000-0002-2752-8265

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