

Article

Nanomaterials in Protection of Buildings and Infrastructure Elements in Highly Aggressive Marine Environments

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Abstract: The 2030 Agenda and Sustainable Development Goals (SDG) are both an engineering challenge and an opportunity. Clean energy (SDG 7), sustainable cities and communities (SDG 11), and climate action (SDG 13) represent an effort to manage, plan, and develop our buildings and infrastructure. The purpose of this study is to contribute to this challenge by analysing nanomaterials in marine environment structures, both urban and maritime. To do this, we have analyzed different regulations of concrete properties in various countries, defining the characteristics of the cement, coating, water/cement ratio, and chloride effect; the difference in durability based on conventional reinforcements and nanomaterials; and use on highly sensitive elements, buildings in marine environments, rubble mound structures, crown walls, and gravity-based foundations for wind power facilities. Division into overhead, underwater, or splash zones entails the use of epoxy resins or silica fume matrices in percentages far below ten percent. Using the most exposed and unfavorable structures, conclusions of application to buildings are established based on the recommendations in maritime engineering most exposed to the actions of the waves. The study concludes with recommendations regarding the durability, increased lifespan, and use of new materials in infrastructure elements in highly adverse marine environments.

Keywords: SDG; building; wind energy; crown wall; nanomaterial; silica fume; splash zone



Citation: del Campo, J.M.; Negro, V. Nanomaterials in Protection of Buildings and Infrastructure Elements in Highly Aggressive Marine Environments. *Energies* **2021**, *14*, 2588. <https://doi.org/10.3390/en14092588>

Academic Editors: Alessandro Cannavale and Adrian Ilinca

Received: 7 April 2021
Accepted: 28 April 2021
Published: 1 May 2021

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1. Introduction

More than ten percent of the world population lives in urban sites located less than 10 metres above sea level [1]. Almost 2.4 billion people, representing 40% of those on the planet, live fewer than 100 kilometres from the coast. Of the 20 most populous cities on the globe—with over five million inhabitants—13 of them are on the sea or close to it [2,3].

Consequently, rising sea levels, extreme events, and climate change constitute a threat. The need for clean energy, is a priority. Sustainable construction, an effort. New materials, a goal.

Most buildings and structures in very aggressive environments are built using reinforced concrete. Their durability is linked to climate and environmental conditions, the characteristics of the materials, and the painstaking and careful construction process through which they are built.

When the concrete—along with its permeability and porosity; the composition of its aggregates, which can facilitate reactions due to chemical transformations; and the framework, which can be affected by corrosion—is analysed, what is found is a progressive loss of mechanical properties, internal progression of chlorides, and gradual deterioration of buildings in areas in proximity to the sea.

Despite the fact that regulations define water–cement ratios, minimal coatings, types of cement, and types of exposure, among other characteristics, concrete in marine environment

construction and maritime facilities experiences considerable problems and has significant shortcomings.

For this reason, a number of additions and additives are required to make it possible to obtain high density, high load-carrying capacity, and low permeability. All of this must be combined with ease of on-site application, proper dosing and the equipment to be used (shuttering, pumping machinery, etc.).

To control corrosion, a structure may have different types of behaviour. It may be in an atmospheric area without direct contact with the sea, only its environment; in a splash zone, on the seafront and subject to violent splashing; in a tidal area, a perimeter wall like a promenade; in an underwater or buried area, footings and deep foundations [4,5] (Figures 1–3).



Figure 1. Buildings progressively damaged by extreme events. March 2014 storm (source: own collection).



Figure 2. Buildings progressively damaged by extreme events. November 2010 storm (source: own collection).

When this occurs, there may be widespread or uniform corrosion; galvanic, due to erosion, due to pitting, progressively damaging buildings or structures.

The solution to these problems is sometimes nanoparticles, generally ceramic nanomaterials, carbon nanocapsules, silica fume, self-repairing coatings that ensure and improve the properties of the material, increasing its durability, and with that, its useful life, minimizing repairs, maintenance, and upkeep during the service period.

There are few studies of its use in buildings in a marine climate, especially in a splash zone, which is why two structural types subjected to wave cycles have been used, such as maritime works (breakwaters, promenades, and crown walls) and facilities to obtain energy from the sea (wind farms).

The aim of this research is to analyze the use of nanomaterials in construction and other maritime structures—such as crown walls, lighthouses, and marine wind power foundations—as vehicles to enable large cities to gain access to clean energy, protecting the planet, based on the SDGs (Figure 4).



Figure 3. Action of the maritime climate on buildings right on the coast (Tacoronte, Spain, 2017). Source: own collection.



Figure 4. Sustainable Development Goals—2030 Agenda [6].

2. Materials and Methods

The research is initially proposed by reviewing the state of the art of the recommendations, rules, and regulations of mass-, reinforced-, and prestressed-concrete, looking at the properties of the materials, the effect on mechanical resistance, and the problems existing in the marine environment.

Next, homogeneous criteria are established for the worst case zones in tidal race and splashes. With this, with this degree of exposure; the loss of the resistance capacity of the sections; and the effect of corrosion, cracking, or fissures among other aspects on them could be determined.

Once this diagnosis has been made, the use of nanomaterials and the different theories based on the percentage as additive, as well as their effects on the resistant properties of concretes, are considered.

Once these aspects have been clarified, the effects of these new materials and the repercussion in the field of civil engineering of buildings and maritime works in the sensitive marine environment can be discussed, checking the values with the experience of the authors in the seven mentioned construction works.

As mentioned in the summary, different regulations in the field of maritime works exposed to waves actions are analysed in order to be able to apply them to buildings in an aggressive marine environment given the scarce number of data on the use of nanoparticles in building structures in the splash zone. Some of the most important requirements for concrete to ensure its durability and to protect structures from highly aggressive marine

environments are found in regulations from different countries. These relate to water–cement ratios, mixture quality, necessary coatings, opening of fissures, aggregate properties, as well as the water-soluble chloride ion content in the concrete.

All these properties are shown in Table 1, which summarizes the properties based on different regulations: Spanish Structural Concrete Instruction (EHE 08) [7,8]; ACI American Concrete Institute standards, Fixed Concrete Structures [9]; British Standards Institution BS 6349 [10]; University of Kyoto [11]; Technical Standards for Port and Harbour in Japan [12]; FIP, Design and Construction of Concrete Sea Structures [13]; and RILEM, the International Union of Laboratories and Experts in Construction Materials, Systems and Structures [14].

Table 1. Basic properties of reinforced concrete in aggressive marine environments. Source: Own elaboration.

Water/Cement	EHE	ACI	BSI 6349	Kyoto	Technical Japan	FIP	RILEM
IIIa, aerial	0.50	0.40	0.65	0.45	0.60	0.45	$0.45 < W/C < 0.50$
IIIb, submerged	0.50	0.45	0.50	0.50	0.55	0.45	$0.45 < W/C < 0.50$
IIIc, splash zone	0.45	0.40	0.45	0.45	0.55	0.40	$0.45 < W/C < 0.50$
Coatings	EHE (mm)	ACI (mm)	BSI 6349 (mm)	Kyoto (mm)	Technical Japan (mm)	FIP (mm)	RILEM
IIIa, aerial	35	50	50 a 75	>25	70	50–70	45 ± 5
IIIb, submerged	35	50	50 a 75	>40	70	50–70	45 ± 5
IIIc, splash zone	40	65	50 a 75	>50	70	50–70	45 ± 5
Chlorides	EHE	ACI	BSI 6349	Kyoto	Technical Japan	FIP	RILEM
content	0.40%	0.15%		0.30–0.60 kg/m ³	0.30 kg/m ³		
Cement/Resistance	EHE	ACI	BSI 6349	Kyoto	Technical Japan	FIP	RILEM
IIIa, aerial	300 kg/m ³	35 Mpa	275 kg/m ³		>24 N/m ³	320 kg/m ³	350 kg/m ³
IIIb, submerged	325 kg/m ³	35 Mpa	350 kg/m ³		>24 N/m ³	350 kg/m ³	350 kg/m ³
IIIc, splash zone	350 kg/m ³	35 Mpa	400 kg/m ³		>24 N/m ³	400 kg/m ³	350 kg/m ³

Table 2 presents the types of cement recommended for maritime and port construction projects, according to the specifications of the Spanish Concrete Instruction EHE 08 [7].

Table 2. Recommended cements for maritime and port construction projects [7].

Type of Exposition	Zone	Maximum W/C	Minimum Cement Content (kg/m ³)	Maximum Water Penetration Depth (mm)	Mean Water Penetration Depth (mm)
IIIa	Marine aerial	0.50	300	50	30
IIIb	Marine submerged	0.50	325	50	30
IIIc	Marine splash zone	0.45	350	30	20

We can see certain discrepancies in both water–cement ratios and in coatings and chloride content, which will affect structures, seafront buildings in aerial environments (IIIa) and splash zone environments (IIIc).

This will affect the corrosion of the reinforcement in pillars, decks, and slabs, foundations and crown walls, and will cause corrosion, fissuring, chipping, cracking, lime stains and loss of coating, resulting in mechanical stress on buildings and structures, chemical attacks, breakage, and gradual deterioration in homes and infrastructure elements (Figure 5).

Engineering provides many mechanisms for preserving steel from corrosion, including barrier coatings, cathodic protection, anodic passivation, electrochemical inhibition, and active corrosion inhibitors.

Ensuring the useful life of our buildings, creating more sustainable cities, with less periodic maintenance and greater durability, requires the use of new materials, among them, nanomaterials.



Figure 5. Fissuring and chipping due to element breakage in a marine environment structure (source: own collection).

Epoxy resins are frequently used due to their ability to adhere to metallic elements and high mechanical, chemical, and impact resistance. Nanoparticles and nanocomposites, notably nanoclays and graphene, improve this performance [15].

Ceramic nanomaterials such as silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), and zirconium dioxide (ZrO_2) are frequently used, adding them to the epoxy matrix, creating a physical and chemical barrier which prevents contact between the metal and the environment. Graphene nanocapsules and nanotubes are another alternative [16].

Having provided this brief description, the study now tackles three aspects. One, buildings and facilities in highly aggressive marine environments; two, materials or nanomaterials for repairs; and three, how to make a city more sustainable using clean energy.

Since in the recommendations, instructions and standards for structural concrete there is no specific articles for the specifications of nanoparticles, different properties improvements have been studied in Table 3.

Table 3. Improvements of concrete with addition of nanoparticles. Source: Own elaboration.

Author	Nano Content (%)	Effect
Khoshakhlegh et al.	0–5%	Increased the strength 4% is the optimum
Ij et al.	0, 3, 5–10%	Increased the compressive strength 3% is the optimum Increased the flexural strength 5% is the followed
Yazdi et al.	0, 1, 3, and 5%	1% and 3% increased the compressive and tensile strength 5% decreased the compressive and tensile strength 3% is the optimum followed by 1%
Nazari et al.	0, 0.50, 1, 1.50–2%	Increased the compressive strength Increased the flexural strength 1% is the optimum followed by 1.50%
Oitulu and Sahin	0, 0.50, 1.25–2.5%	Increased the compressive strength at 3 and 7 days 0.50% is the optimum

3. Results

As mentioned above, the main aim for buildings and infrastructure elements in highly aggressive marine environments is to prevent corrosion, increasing their useful life, thus ensuring durability and minimizing upkeep and maintenance costs [17].

For buildings and structures in a marine environment to perform suitably, it is necessary to establish a number of criteria to enhance their durability based on the following aspects: one, use of new materials to replace steel; two, augmenting the coating, that is, its

thickness if conventional reinforcement is still used; three, improvements to the cement matrix to obtain less permeable concretes, hindering the penetration of aggressive agents, especially chlorides; and lastly, improving abrasion resistance.

Often, more in repairs on buildings and structures damaged by the aggressive marine environment—such as crown walls or the caissons of vertical dikes or caisson quays—corrosion inhibitors are used, such as a hardened concrete priming barrier.

This is not the case under discussion here, but sometimes, four different families of stainless steel are used—*austenitic*, *ferritic*, *duplex*, and *martensitic*—as well as fibreglass-reinforced plastic bars. However, in the case of nanomaterials, the cement matrix is the source of their functioning and improvement. In the dimensional range of 1–100 nanometres (nm), the materials have properties which are of considerable interest due to their applications in engineering and other fields of science, making it possible to obtain more durable, sustainable, affordable elements, providing a boost for the construction industry.

They have a very high surface-area-to-volume ratio with an increase in their relative surface area, as well as a very high number of surface atoms. When they are added to the cement matrix, this increases hydration speed, ups the amount of calcium silicate hydrate (CSH), the gel produced due to the pozzolanic relationship with calcium hydroxide ($\text{Ca}(\text{OH})_2$), reduces porosity, and improves mechanical properties. In the field of marine engineering, nanosilica, nano SiO_2 (NS); nanotitanium, nano TiO_2 (Nti); nanoaluminium, nano Al_2O_3 (NA); and nano Fe_2O_3 (NF) additions have been incorporated, achieving spectacular results in highly aggressive environments.

As Reches [18] states, there is no easily identifiable dependence of the properties of nanomaterials on the properties of concretes, especially the water–cement ratio and the use of additives. Recommendations for improving strength in the laboratory are between 5% and 10%. However, from experience on the mound with a layer of antifer blocks in Ashdod, Israel where heavy concrete with nanosilica was used, on the dike at Point Langosteira in A Coruña, and on Oresund Bridge, values below 5% were achieved, closer to 1–3%. To improve strength at early ages, it is advisable to mix in fly ash, blast furnace slag, or ceramic waste.

The circulation or dissemination of ions through the mixture is a mechanism by which concrete is corroded due to sulphate attack, chloride intrusion, alkali–silica reaction, acid corrosion, or carbonatation. Therefore, delaying this intrusion makes it possible to extend the useful life of the base material. Today, international projects propose minimum useful lives in excess of 100 years, meaning that treating concrete and the use of nanomaterials are considered essential.

When nanosilica is used, the extremely small size of the particles and their dispersion make it difficult to achieve a homogeneous distribution in the concrete mixture. Special care must be taken, starting by mixing the water with superplasticizer, then incorporating the nanoparticles, and finally, adding this liquid mixture to the other solid components.

The reaction capacity is very high, although not all nanomaterials can be hydrated, with nanosilica having this advantage over other composites.

This can function in one of two ways. If it dispersed well, the result is a dense microstructure. Otherwise, there are voids or weak spots. Acceleration of the hydration of the plaster and rapid calcium hydroxide formation in the initial stages are seen if NS is included, decreasing the setting time of the concrete. Higher hydration heat and faster dissolution of the tricalcium silicate are also identified.

Graphene oxide, or graphene nanoplatelets, is also usually used as a cement-derived materials additive. This is a two-dimensional sheet derived from carbon in a honeycomb panel and atoms in an sp^2 lattice. It enhances the mechanical, thermal, and electrical properties, also improving thermal diffusivity and electrical conductivity. Its high specific surface area provides an extensive area of contact, with a significant bond between components of the matrix and a dense structure.

In this case, a value of less than 0.50% is recommended. However, Chang [19] includes 0.40% and is able to improve flexural strength and compressive strength by 6% and 5%, respectively. Wang demonstrated that 0.05% also made it possible to increase the strengths by 71% and 24%, there being numerous experiences with a variety of results. There have been many tests and experiments with different properties of concrete—generally with water–cement ratios of 0.66, considerably different from the classic ratios in marine environments (0.45–0.50)—seeking to optimize the mechanical properties through the formation of covalent bonds in the graphene interface and cement matrix, obtaining no conclusive results in the field of marine engineering.

Similarly, there are very preliminary studies with nanoclays. These are hydrated aluminium silicates whose structure is sheets of SiO₄ tetrahedrons linked by their edges to another three, forming a hexagonal grid. Kaolinite, montmorillonite, or vermiculite are normally used, based on the quantity of silica in their chemical composition, sheet structure, surface area, and impermeability to water and gases. With cement and concrete, they are very limited, focused on nano kaolin, which in percentages of less than 10% improved compressive strength by more than 10% and tensile strength by 2–10%.

Engineering and technology now have what are known as “smart coatings”, which adapt to external stimuli and provide suitable responses [20,21]. Antifouling paint, self-curing paint and paint with nanocapsules are a few of these [22]. These materials can be manufactured using top-down processes, in other words, at a normal scale and then reduced to nanometric; or bottom-up, done atom to atom, molecule to molecule [23].

If it is necessary to repair a building or structure, it is also possible to use two techniques. The first consists of adding polymeric nanocapsules [24]; the second is using inhibitors [25]. If nanoparticles are used, it is common to add them to an epoxy resin, decreasing the electrolyte’s paths of diffusion to the substrate.

When the nanoparticles are ceramic, they can be employed using a wet process to form a dispersion and then applied, or to be applied directly to the ceramic element using a dry process [26].

Traditional industrial solutions involve painting methods. On major marine wind power or wave energy projects, three coats are usually applied, with thicknesses of approximately 60, 100, and 60 µm [27].

The first of these is the most important, as it is the coat that serves to connect the substrate (generally steel) to the subsequent coats. For this reason, it is necessary to ensure that this coat adheres to the surface of the element (60 µm) as well as possible. Next, the second intermediate coat of epoxy is applied. This will be the coat that prevents the corrosion, given that it is the thickest (100 µm). And lastly, for appearance, a topcoat (60 µm) is applied, which generally adds color and pigmentation to the system, as well as gloss and other characteristics. In Figure 6, the difference can be clearly seen, along with the different types of foundations in marine wind power, floating, and gravity [23], while in Figure 7, it is not possible to clearly see the glossy paint of the third coat.

Because of this, advances in the material—or better said, nanomaterial—with the improvement in the cement matrix (from metakaolin, nanoparticles such as nanoclays, graphene oxide, powdered or liquid nanosilica, silica fume or combinations of these); improvements in the abrasiveness of specific aggregates, silica fume in the matrix or the use of non-metallic fibers; and lastly, corrosion inhibitors with additives in the mixture—enable offshore buildings, facilities, and structures to achieve durability levels in excess of 50 years, considerably higher than minimum useful lives.

To summarize, we include the effects of nanoparticles on concrete, in Figure 8, as presented by Reches in his recent 2018 article, published in *Construction and Building Materials*, a basic reference for comparing the use of conventional concrete and concrete with added nanoparticles of all kinds [18], as well as how nanoparticles perform within a cement matrix [30].



Figure 6. Aerial photo of the Elisa Project, Elican, Arinaga, and Gran Canaria Island [28].



Figure 7. Difference between a GBS and a floating structure (Marinero 2018) [29].

	Concrete (with no NPs)	Effect of NP addition
Components	• OPC • Water • Fine aggregate (sand) • Coarse aggregate (gravel) • May contain admixtures (chemical, mineral or fiber) and entrained air	• Nano-scale (typically 4–40 nm) particles of SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaCO_3, clays or other solid phases
Properties of fresh concrete	• Workability/flowability (required for successful casting) • Cohesiveness (i.e., tendency to avoid segregation of concrete into components) • Content of entrained air in concrete (may be advantageous or disadvantageous) • Setting times: - Initial (i.e., time when concrete can no longer be worked) - Final (i.e., time when concrete has more than zero nominal compressive strength)	• Reduce workability/flowability • Increase cohesiveness • May increase or decrease air content • Shorten setting times
Hydration reactions	• Hydration of OPC into C-S-H and other hydrates (Eq. (1)) • Pozzolanic reaction (i.e., reaction of mineral admixtures with CH from OPC hydration, which produces secondary C-S-H per Eq. (2)) • Hydrates (primarily C-S-H) form solid networks and bind aggregates into a matrix	• Nucleate the hydration of OPC and the pozzolanic reaction of mineral admixtures (catalytic role of NPs) • May be pozzolanic (intrinsic reactivity of NPs) • May pack between larger particles (e.g., OPC), and reduce defect size
Properties of hardened concrete	• Mechanical - Compressive strength (i.e., design strength for structural purposes) - Tensile/flexural strength (indicates tendency for cracking) - Modulus of elasticity (determines strain for a given stress) • Durability - Durability to weathering: determined primarily by diffusivity to gases/ions (via porosity, pore size distribution, pore connectivity) - Durability to elevated temperatures	• Generally (with notable exceptions) increase mechanical properties, esp. at early ages • Generally reduce diffusivity and enhance durability

Figure 8. Impact of nanoparticles on concrete [18].

Also, Figure 9 refers to how nanosilica behaves within the cement matrix [19] and how properties of these concretes improve.

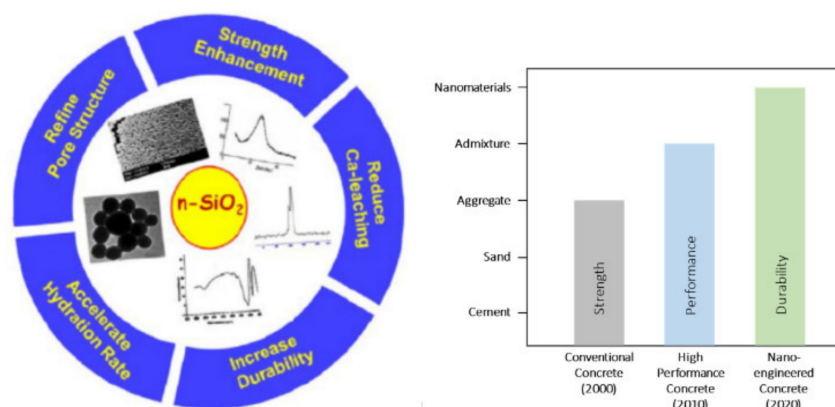


Figure 9. How nanosilica behaves within the cement matrix [19] and improved properties (source: own elaboration).

4. Discussion

To obtain clean energy in coastal cities, it is common to utilize marine wind facilities. These may have different types of foundations, as shown in Figure 10.

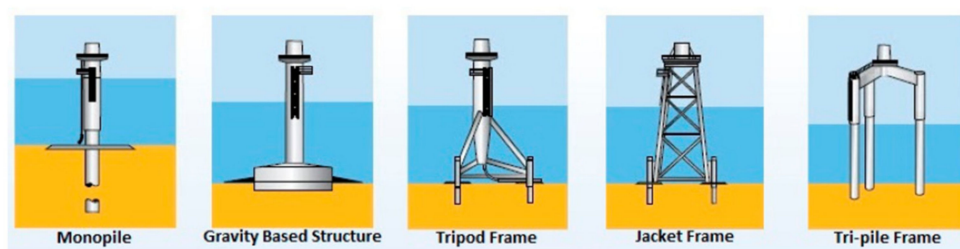


Figure 10. Main types of direct foundations in offshore wind energies [28].

Gravity-based foundations (GBS) have concrete with added silica fume (90% SiO_2), with a dosage of 5–10% of the weight of the cement to obtain strengths on the order of 70–100 MPa [8].

Silica fume, also referred to as microsilica or active silica, is an inorganic product in the form of extremely fine round particles produced during the reduction of quartz with carbon in the process of obtaining silicon metal and ferrosilicon in electric arc furnaces. It is made up of amorphous silicon dioxide. It has a high pozzolanic capacity, as it is a very fine material and rich in silica. It combines with the calcium hydroxide in cement to form calcium silicate hydrate, functioning from the initial stages or early ages, from the second day.

This makes it possible to obtain high-strength, high-durability, high-permeability concrete, and pumping adjuvant. On site, they are very easy to distinguish because the concretes are darker, they require more water, reducing their exudation.

The mixtures perform very well in terms of freeze-thaw resistance; resistance to chemical attack due to their low permeability; they are beneficial to the alkali–aggregate relationship; they have considerable abrasion resistance and respond well to sulphates and chlorides.

Despite the advantages described, the use of silica fume results in less workability and requires cleaner shuttering. As pumping systems are generally used in construction and infrastructure, the percentage of 5–10% must be reduced by 1–3% of the total weight of the cement to make it easier to pump the concrete, achieving stability and improving resistance. This is highly beneficial in structures—such as unique buildings, promenades, walls, and crown walls—among other works in sustainable cities [29,31].

This ensures the durability of the foundations of wind farms, both gravity-based and floating or piled, which in 2019 added 6.1 GW of capacity to the industry, exceeding the 4.5 GW added in 2018, contributing 10% of all wind power and producing a cumulative total of 29 GW [30].

The 2030 Agenda and the Sustainable Development Goals (SDG), especially 7, clean energies, is observed in their growth from the period 2010–2016 to 2017 to 2040, as shown in Figure 11, demonstrating the commitment to save the planet and reduce greenhouse gases and global warming.

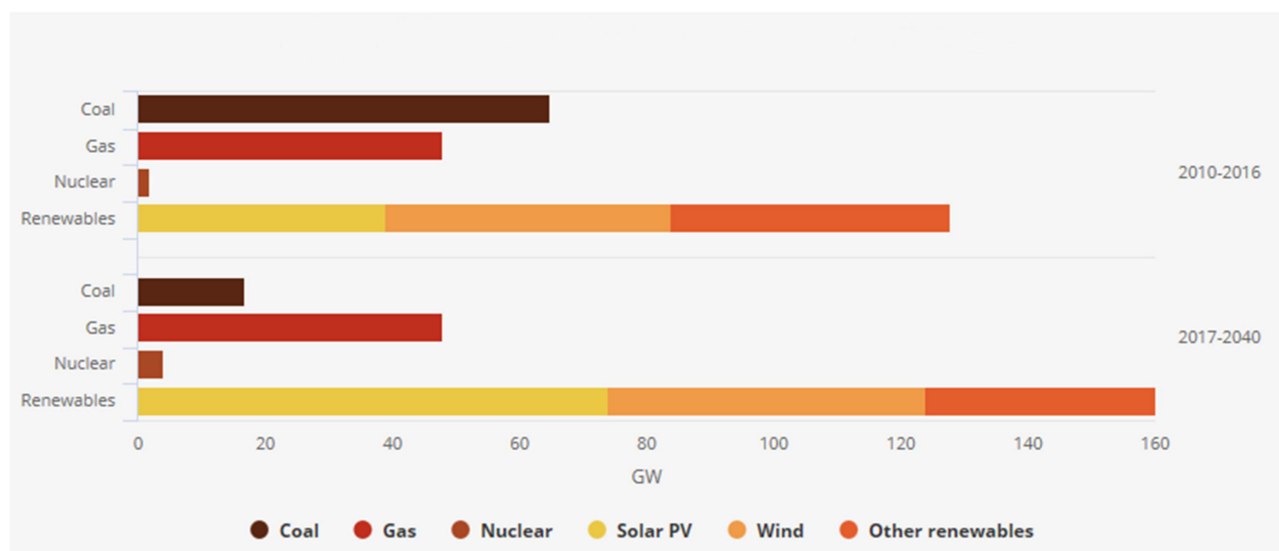


Figure 11. World annual average increase -in GW- of the main energy sources [32].

In foundations with monopiles, manufactured in steel, which represent more than 80% of all foundations, it is considerably easy for oxidation to occur in marine environments, with a loss of over 1000 g/m² in weight and 0.55 mm in thickness at 5 years; almost 2 mm at 25 years; reaching 7.50 mm at 100 years (EN 1993-5, 2007).

For this reason, to achieve clean energy and sustainable cities in highly aggressive marine environments, the structures, buildings, and facilities may have additional costs ranging from 10% to 25%, together with the additional effort to protect the materials to ensure durability. Today, organic coatings such as paints are used, sacrificial anodes, given that they are materials which corrode before the steel (Zn, Mg, Al), thus preventing its deterioration [33].

In this case, it is also advisable to utilize nanomaterials to improve the mechanical, physical, and chemical properties of these devices, creating a more sustainable planet. The different types of nanomaterials, their percentages and the improvements in concrete properties are shown in Table 4.

Table 4. Variation of compressive and flexural strengths based on the added percentages (source: own elaboration)

Nanoparticles	Compressive Strength	Flexural Strength
Nanosilica (<3%)	>12%	>3%
Nanotubes (<10%)	>15%	>20%
Fibers	>5%	>10%

This is a great opportunity to meet the climate goals, replace fossil fuels, provide new and inexhaustible materials for use, and foster clean energies based on movements of the sea and atmosphere.

The first work to be carried out with additions of nanomaterials was the Monjuic pedestrian walkway in Barcelona in 1992. Multiple applications with high-strength concrete followed, until finding fluvial or maritime environments such as the walkway over the Guadalete river in the Port of Malaga (1992), the footbridge over the river Miño in Galicia (1995), the residential complex of Natura Playa, a building on the beachfront in Alicante (1996) or the mantle blocks of the Langosteira dam in A Coruña in 2005 (Figure 12).



Figure 12. Own experience in nanomaterials works (source: own elaboration).

Today, new materials are also starting to replace concrete in our seaside cities. We need only to cite the construction of a lighthouse with composite materials in Valencia, Spain (2015) and the screed on a crown wall on a dike in Escombreras, Spain (2017) with fiberglass-reinforced polyester reinforcement (Figure 13).



Figure 13. Composite materials lighthouse in Valencia (2015) and screed of the crown wall in Escombreras with FRP (2017) (source: own collection).

5. Conclusions

Buildings and civil engineering works in Spain are subject to different environments: aerial, splash zone, submerged or buried, meaning they may sustain fissuring, corrosion, chipping, and cracking, progressively damaging them, in addition to having an extremely negative visual impact. Derived from the regulations, water-cement ratio is proposed to be less than 0.50; cement weight must be more than 350 kg/m^3 , and coating in the reinforced concrete greater than 65 mm, with an aggregate size of 20 to 40 mm and a chloride content less than 0.30, to obtain a compressive strength greater than 210 kg/cm^2 or 21 N/mm^2 .

Utilizing nanomaterials is a solution for repairing these, with ceramic materials being recommended, applied using either a wet process or dry process, or adding silica fume in percentages between 1% and 3%. All of this improves protection of the reinforcement and increases resistance.

The experience in the use of nanosilica with percentages lower than 3% allows to increase the resistance to compression by more than 10% and to bending by more than 3% in the short term (three days).

Experience in the use of nanotubes with percentages lower than 10% allows the resistance to compression to be increased by more than 15% and to bending by more than 20% in the short term (three days).

Experience in the use of concrete with fibers allows to increase the resistance to compression by more than 5% and to bending by more than 10% in the short term (three days).

This situation also adds durability to structures in a marine environment, decreases their maintenance and slows down the progression of rust in conventional steel reinforcement due to the micro pores existing in the concrete during its installation in an aggressive environment.

The economic evaluation of these concretes makes the works more expensive when it comes to large volumes, having to obtain an economic optimum in the study processes and service phases of the same.

It is advisable to utilize bottom-up techniques or the creation of atom to atom, molecule to molecule materials when using nanomaterials on buildings and infrastructure elements in marine environments.

Despite the fact that they represent an additional cost, increased durability and lack of maintenance and upkeep during the useful life make it advisable to use them, given the aggressiveness of the actions and the recurrence of extreme events.

Author Contributions: This paper will be included in the Research Program of ECOREL Group, Environment, Coastal and Ocean Research Group, Technical University of Madrid. The structural and materials discussion and qualifications were done by Full V.N. and Associate J.M.d.C. The cases studies were prepared by V.N. and J.M.d.C. Finally, the comparison between techniques was done by J.M.d.C. and V.N. The authors contributed toward choosing adequate figures and references to provide an accurate paper. Conceptualization, V.N. and J.M.d.C.; Funding Acquisition, Investigation, Methodology, Writing—Original Draft, and Writing—Review and Editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jevrejeva, S.; Jackson, L.P.; Grinsted, A.; Lincke, D.; Marzeion, B. Flood damage costs under the sea level rise with warming of 1.5 C and 2 C. *Environ. Res. Lett.* **2018**, *13*, 074014. [CrossRef]
2. Portnov, B.A. On Locational Commonalities of Largest Cities Worldwide. In *Innovations in Urban and Regional Systems*; Springer: Cham, Switzerland, 2020; pp. 23–48.
3. Small, C.; Nicholls, R. A Global Analysis of Human Settlement in Coastal Zones. *J. Coast. Res.* **2003**, *19*, 584–599. Available online: <http://www.jstor.org/stable/4299200> (accessed on 8 December 2020).
4. Ding, K.; Guo, W.; Qiu, R.; Hou, J.; Fan, L.; Xu, L. Corrosion behavior of Q235 steel exposed in deepwater of South China Sea. *J. Mater. Eng. Perform.* **2018**, *27*, 4489–4496. [CrossRef]
5. Jia, J.; Cheng, X.; Yang, X.; Li, X.; Li, W. A study for corrosion behavior of a new-type weathering steel used in harsh marine environment. *Constr. Build. Mater.* **2020**, *259*, 119760. [CrossRef]
6. United Nations. Sustainable Development Goals. Available online: <http://www.un.org/sustainabledevelopment/sustainable-development-goals/> (accessed on 25 November 2020).
7. EHE. *Instrucción de Hormigón Estructural*; Ministerio de Fomento: Madrid, Spain, 2008.
8. Eurocódigo EC-1. *Bases de Proyecto y Acciones en Estructuras*; UNE: Madrid, Spain, 1992.
9. API. *Guide for the Design and Construction of Fixed Offshore Concrete Structures*; American Concrete Institute: Farmington Hills, MI, USA, 1984; p. 357R-84.
10. British Standards Institution. *BS 6349. Maritime Works*; BSI: London, UK, 2019.

11. University of Kyoto. *Fundamentals of Durable Reinforced Concrete*; Kyoto University Press: Kyoto, Japan, 2012.
12. *Technical Standards for Port and Harbour Facilities in Japan*; Overseas Coastal Area Development Institute of Japan: Tokyo, Japan, 1980.
13. FIP Recommendations. *Design and Construction of Concrete Sea Structures*; Thomas Telford: London, UK, 1985.
14. International Union of Laboratories and Experts. *Construction Materials, Systems and Structures (RILEM)*. 289—DCM: Long-Term Durability of Structural Concretes in Marine Exposure Conditions; RILEM: Madrid, Spain, 2019.
15. Alaejos, M.P.; Bermúdez, M.A. Monografía 96. In *Corrosión De Las Armaduras En El Hormigón Situado En Ambiente Marino*; Centro de Estudios y Experimentación de Obras Públicas, CEDEX: Madrid, Spain, 2008.
16. Bermúdez, M.A.; Alaejos, M.P. Monografía 103. In *Estudio Experimental De La Durabilidad Del Hormigón Armado En Ambiente Marino. Zona Sumergida Y De Carrera De Marea*; Centro de Estudios y Experimentación de Obras Públicas, CEDEX: Madrid, Spain, 2009.
17. EAE. *Instrucción de Acero Estructural*; Ministerio de Fomento: Madrid, Spain, 2011.
18. Reches, Y. Nanoparticles as concrete additives: Review and perspectives. *Constr. Build. Mater.* **2018**, *483–495*. [[CrossRef](#)]
19. Chang, T.P.; Sun, Y.M.; Ming, T.L. Service Life Prediction for Concrete Structures by Time-Depth Dependent Chloride Diffusion Coefficient. *J. Mater. Civ. Eng.* **2010**, *22*, 11.
20. Chang, T.C.; Cao, X.; Bao, S.H.; Ji, S.D.; Luo, H.J.; Jin, P. Review on thermochromic vanadium dioxide based smart coatings: From lab to commercial application. *Adv. Manuf.* **2018**, *6*, 1–19. [[CrossRef](#)]
21. Aklujkar, P.S.; Kandasubramanian, B. A review of microencapsulated thermochromic coatings for sustainable building applications. *J. Coat. Technol. Res.* **2020**, 1–19. [[CrossRef](#)]
22. Gao, Q.; Wu, X.; Zhu, R. Antifouling energy-efficient coatings based on BiOClxBr1–x microflowers: NIR reflective property and superhydrophobicity. *Constr. Build. Mater.* **2020**, *257*, 119569. [[CrossRef](#)]
23. Carro Rodríguez, J. TFM Universidad De Oviedo. *Máster Interuniversitario En Integridad Estructural y Durabilidad De Materiales, Componentes Y Estructuras*; University of Oviedo: Oviedo, Spain, 2014.
24. Shah, K.W.; Huseien, G.F. Biomimetic Self-Healing Cementitious Construction Materials for Smart Buildings. *Biomimetics* **2020**, *5*, 47. [[CrossRef](#)] [[PubMed](#)]
25. Jia, Y.; Qiu, T.; Guo, L.; Ye, J.; He, L.; Li, X. Preparation of pH responsive smart nanocontainer via inclusion of inhibitor in graphene/halloysite nanotubes and its application in intelligent anticorrosion protection. *Appl. Surf. Sci.* **2020**, *504*, 144496. [[CrossRef](#)]
26. Santos, S.C.; Rodrigues, O., Jr.; Campos, L.L. Dispersion of thulium-yttria nanoparticles to build up smart structures. *Mater. Today Commun.* **2020**, 101749. [[CrossRef](#)]
27. Mutsuda, H.; Tanaka, Y.; Patel, R.; Doi, Y.; Moriyama, Y.; Umino, Y. A painting type of flexible piezoelectric device for ocean energy harvesting. *Appl. Ocean Res.* **2017**, *68*, 182–193. [[CrossRef](#)]
28. Luengo Frades, J.; García Barba, J.; Negro, V.; Martín Antón, M.; López-Gutiérrez, J.S.; Esteban, M.D.; Moreno Blasco, L.J. Preliminary Design for Wave Run-Up in Offshore Wind Farms: Comparison between Theoretical Models and Physical Model Tests. *Energies* **2019**, *12*, 492. [[CrossRef](#)]
29. Marinero, M. *Eólica Marina Flotante: Análisis, Principales Prototipos y Prospección de Futuro*. Master's Thesis, Technical University of Madrid, Madrid, Spain, 2018.
30. Singh, N.B.; Sachan, D.; Verma, R.; Jayaganthan, R.; Kumar, A. Mechanical behavior of 304 Austenitic stainless steel processed by cryogenic rolling. *Mater. Today Proc. Switz.* **2018**, *5*, 9. [[CrossRef](#)]
31. Fernández García, S. *Corrosión de Armaduras en el Hormigón Armado en Ambiente Marino*. Tesis Doctoral. Escuela Técnica Superior de Ingenieros de Caminos, Canales y Puertos; Directora: María Pilar Alaejos; Universidad Politécnica de Madrid: Madrid, Spain, 2016.
32. Windeurope 2019. World Annual Average Increase (in GW) of the Main Energy Sources Currently Available. Offshore Wind. Available online: www.offshorewind.biz (accessed on 2 April 2021).
33. Ministerio Para La Transición Ecológica. Available online: <https://www.miteco.gob.es/es/> (accessed on 4 April 2021).