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Application of residuals from purification of bivalve molluscs in Galician to facilitate marine ecosystem resiliency through artificial reefs with shells – One generation

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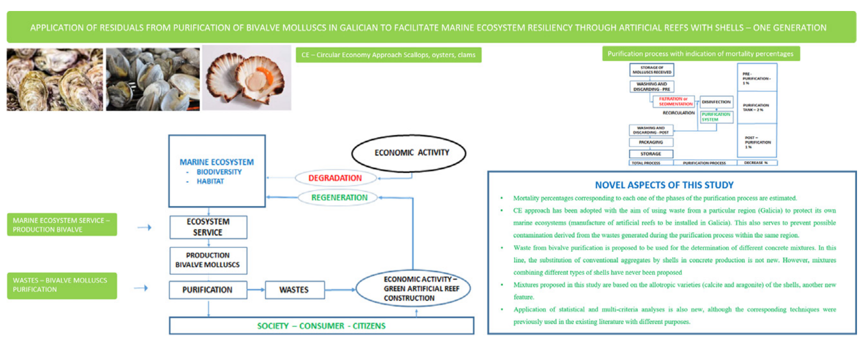
HIGHLIGHTS

- Waste from seashells is proposed as aggregates for concrete.
- The granulometry, specific gravity and composition of seashells were characterized.
- A statistical analysis on the compressive strength and water absorption was realized.
- A multi-criteria analysis was carried out to complement the statistical analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

The seas and oceans of the planet provide a wide range of essential resources. However, marine ecosystems are undergoing severe degradation due to the unsustainable exploitation and consumption patterns of the linear economy. On the other hand, many economic activities linked to the sea generate a large amount of waste, leading to negative impacts, such as the cost of treating or disposing of this waste. A case in point is bivalve mollusc production: a purification process is needed to avoid the risk of diseases through faecal contamination. The present work proposes an innovative procedure to convert this waste, calcium carbonate as calcite and aragonite allotropic types, into by-products. These by-products can be used to manufacture green artificial reefs, partially replacing concrete aggregates with a sustainable alternative to the geological sources of $CaCO_3$. By installing these reefs, marine ecosystems could be created in a sustainable way and an innovative approach based on the circular economy could be taken towards protecting them. To this end, different concrete mixtures with bivalve shells are proposed. Although this study had been carried out for Galicia (NW Spain), the methodology followed could also be valid for other regions. A physicochemical characterisation of the waste from purifying the bivalves, including oysters, mussels, clams and scallops, was performed. Statistical and multi-criteria analyses were done in order to select the best dosage. Both have provided justification for using a mixture of shells with a predominance of calcite (oyster, scallop) instead of shells with a predominance of aragonite. The multi-criteria analysis served to identify the two best alternatives with dosages in which the medium aggregates were substituted with shells mainly from oysters, with a predominance of calcite. Finally, the statistical analysis played a role in estimating the compressive strength and water absorption of each mixture from the design parameter values.

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1. Introduction and objectives

The health of our oceans directly impacts humanity (Rashid Sumaila et al., 2016). One key outcome is variation in the supply of essential resources such as food, minerals and energy (Visbeck et al., 2014). The expected growth in population will considerably increase our dependency on the oceans. A possible way to cope with this challenge is to encourage the sustainable cultivation of seafood products.

Nevertheless, ecosystems will continue to degrade unless economic activities (Lotze et al., 2018), particularly those involving the extraction and overexploitation of resources (Rickels et al., 2016), is efficiently regulated. In the name of sustainable development, special attention must be paid to renewable marine resources (FAO, 2017) through the conservation and management of the ecosystems and the services they produce. Among their multiple contributions, bivalves represent 14 % of worldwide marine production. This growing production trend goes hand in hand with consumption, which has risen from 10.7 in 1999 to 17.5 million tonnes in 2018 (FAO, 2020; APROMAR, 2021). These quantities (89 %) are produced through aquiculture, while the remaining percentage corresponds to wild species fisheries (Wijsman et al., 2019).

Regarding species, the FAO (Food and Agriculture Organisation of the United Nations) provides a list of commercially available marine bivalves grouped into five types: oysters, clams, scallops, mussels and abalones (Wijsman et al., 2019). However, in practice, worldwide production mainly comprises the first four types (Alonso et al., 2021).

The aquiculture species vary greatly depending on the continent and region, Table 1. Nevertheless, their production percentages for the last 15 years have had a stable distribution (Alonso et al., 2021). Globally, China (85 %) seems to be much more significant than the remaining producers (Alonso et al., 2021), while Europe represents a modest 3.8 %, with its production mostly based in three countries: Spain (mussels), France (oysters) and Italy (clams) (APROMAR, 2021).

It is worth mentioning that Galicia is responsible for 40 % of European production and also for 15 % of the worldwide production of cultivated mussel (Labarta and Fernandez-Reiriz, 2019). Galicia has a longstanding mussel processing industry (Barros et al., 2009; Labarta and Fernandez-Reiriz, 2019), although this tradition has its environmental costs (Carral et al., 2019; Carral et al., 2021a). It is important to add that, in Galicia, >50 % of the population lives in coastal zones where there is substantial maritime activity.

However, with the development of conservation techniques and logistics, there has been growing consumption of bivalves produced in remote waters. This trend gives rise to new challenges regarding food safety, particularly related to eliminating pathogen microorganisms (FAO, 2010). Molluscs that are mainly consumed raw or alive, such as oysters, or undercooked, such as mussels, constitute a major risk, and rigorous control measures are crucial (Fajardo et al., 2014; Fernández et al., 2016).

Consequently, the protection of the consumer must be guaranteed in two ways: 1- purification, which employs the natural filtering activity of bivalves to eject the intestinal content (Rodney et al., 2007; Polo et al., 2014); limiting the accumulation of pathogen bacteria, virus, toxins and chemical pollutants (Bellou et al., 2013; Biessy et al., 2019); 2- monitoring and controlling the production areas in order to detect the presence of products that may carry pathogens.

Table 1
Distribution of the bivalve production in different regions. Mussels are the main species produced in Europe, while oysters and clams prevail in Asian production. Source: as indicated.

% of production	China	Europe – 28	Galicia
Mussels	5.8	63.2	99.1
Oysters	33.3	14.7	0.5
Scallops	12.1	14.7	0.1
Clams	30.5	7.4	0.3
Source	(Mao et al., 2019)	(Wijsman et al., 2019)	(APROMAR, 2019)

Galicia is no exception to this problem (Table 2), as the bivalve molluscs captured in the Galician estuaries present the pollutants that remain in their waters.

Regulations in developed countries are mostly concerned with the purification process. Nevertheless, many researchers, such as Martínez-Albores et al. (2020) or Love et al. (2010), question the effectivity of this process and propose ways of improving its efficiency and obtaining safe food (Martínez-Albores et al., 2020). In Section 1 of Appendix A, the reader can find further information about the purification process. The mortality percentages corresponding to the pre-purification, purification and post-purification stages- 1, 2, and 1 % respectively- were estimated through a field study in a purification plant (Appendix A).

This process is essential, but it also produces a large amount of waste from shells. Managing this waste is a major concern for the regions rich in bivalve production. Therefore, finding a way to use these shells for any application that helps protect or enhance marine ecosystems and their habitats and biodiversity is of paramount importance.

However, oceans are not only a source of food and economic activity. They also constitute the main sink of anthropogenic carbon, since they capture one third of the total anthropogenic CO_2 emissions to the atmosphere (Sabine et al., 2004; Gruber et al., 2019). Numerous human activities take place in the coastal and open ocean. Alonso et al. (2021) argue that only a few of these activities can contribute to CO_2 sequestration: shellfish aquiculture is one of them. Furthermore, aquiculture activity involving bivalves has a low carbon footprint and that may further reduce the atmospheric CO_2 sequestered through the calcic carbonate ($CaCO_3$) contained in the shells (SARF (Scottish Aquaculture Research Forum), 2012). The mussels cultivated on hang ropes or floating platforms produce a cradle-to-gate carbon footprint lower than 500 kg of CO_2 eq./t of mussels (Iribarren, 2010; SARF (Scottish Aquaculture Research Forum), 2012). This quantity may rise to around 1500 kg CO_2 eq./t in the case of oysters cultivated on intertidal sandbanks (SARF (Scottish Aquaculture Research Forum), 2012) or in the case of scallops captured through dredge systems (Cortés et al., 2021; Tamburini et al., 2019). These footprint values are extremely low if similar activity, such as fish aquaculture, is considered (Alonso et al., 2021).

Thus, there are multiple reasons for protecting marine ecosystems from the degradation they are experiencing and, at the same time, for improving the production of their services (Carral et al., 2021b, 2022). In this sense, artificial reefs (ARs) stand out as an interesting option. These reefs are structures built in coastal areas in an effort to modify the ecosystem (Kim et al., 2017). These ARs play a role in fishery management, coastal protection, mariculture and tourism. They also help with improving production, preserving biodiversity, rehabilitating habitats, creating sea afforestation, protecting habitats, reducing poaching and promoting sports, like diving and recreational fishing, (Kim et al., 2019).

The first steps aimed at modifying the ecosystems through ARs took place in the 1970s (Silva Lima et al., 2019), when economic growth was based on a linear production model. However, this linear model is not feasible in a planet with finite resources and a limited capacity to absorb wastes (Bonciu, 2014). For this reason, the circular economy (CE) has been emerged over the past decade (Blomsma and Brennan, 2017) as a general concept. It proposes an economic system in which resources are efficiently employed and the flow of energy and materials are limited and closed (Bocken et al., 2016; EC, 2015a; EC, 2015b).

Within this framework, several researchers (Huang et al., 2016; Liu et al., 2017; Carral et al., 2018) are making an effort to enhance the role of green ARs – GARs (Green Artificial Reefs). These are hybrid-type reefs as they are halfway between artificial and natural structures. GARs are designed to employ natural resources in a suitable way and to reduce both energy consumption and emissions, according to the principles of CE.

Along similar lines, the production of ARs using waste materials (by-products from the purification stations) combined with reinforced concrete (Bell et al., 1989; Gu, 2005; Carral et al., 2020; Lamas Galdo et al., 2022) is an interesting option that should be explored.

In other words, the main objective of this study is to analyse the application of CE to both the purification process of bivalves and the

Table 2
Bivalves that must be compulsorily treated in Galicia and annual purification quantities. Source: own source according to Pescadegalicia, n.d. and Cortés et al. (2021).
(1) Pescadegalicia, n.d.
(2) Cortés et al. (2021).

Commercial name	Scientific name	Purification (tonnes)				
		2017	2018	2019	2020	Total 2021
Mussel (1)	*Mytilus edulis, Mytilus galloprovincialis*	266,925.7	278,702.9	255,517.9	232,761	232,761
Oyster (1)	*Ostrea edulis*	304.348	325.256	394.036	267.950	732.641
Scallop (1)	*Crassostrea angulata*	379.296	428.567	522.656	454.691	
Slimy clam (1)	*Venerupis pullastra*	248.968	247.428	303.585	125.457	1617.877
Fine clam (1)	*Venerupis decussatus*	163.513	144.190	186.777	158.865	
Japanese clam (1)	*Ruditapes philippinarum*	1276.036	1090.485	1415.263	1333.555	
Cockle (1)	*Cerastoderma edule*	508.718	348.780	623.240	475.578	475.578
Scallop (2)	*Pecten maximus*	35.000	118.000	132.000	83.000	83.000

manufacture of ARs. In particular, one of the goals is to incorporate the calcium carbonate ($CaCO_3$) contained in shells from bivalve purification into concrete. This concrete will be employed to manufacture green ARs to mitigate the degradation of marine ecosystems, as shown in Fig. 1. More specifically, shells will be used as a sustainable alternative to non-renewable geological sources of $CaCO_3$, such as limestone (Alonso et al., 2021). This is of great relevance as the CO_2 sequestrated by $CaCO_3$ minerals was emitted to the atmosphere when it had not been altered by human activity. In contrast, the CO_2 sequestrated by $CaCO_3$ from bivalve mussels can be linked to an atmosphere degraded by human activity.

Different concrete mixtures were considered in this proposal. All of these mixtures were thus subjected to a range of mechanical tests and the obtained results were used to perform both statistical and multi-criteria analyses. To the best of the authors' knowledge, no research along similar lines can be found in the existing literature. In particular, the innovative aspects of this study are:

- This the first time that the mortality percentages corresponding to each of the purification process phases have been estimated.
- This is also the first time that bivalve purification waste has been used in the effort to determine the most suitable concrete mixtures. While replacing conventional aggregates with shells in concrete production has been mooted in other studies, mixtures combining various types of shells have not. Moreover, the mixtures proposed in this study are based on allotropic (calcite and aragonite) shell varieties.
- Another innovation is that a CE approach is adopted with the aim of using waste from a particular region (Galicia) to protect that region's own marine ecosystems and manufacture artificial reefs to be installed there. This process prevents possible contamination derived from the waste generated during the purification process within the same region.
- For these specific tasks mentioned above, the application of both statistical and multi-criteria analyses is also new, although these techniques have been previously used for different purposes in the existing literature.

The rest of the article is structured as follows. The procedure underpinning this study is described in Section 2 (Material and Methods). Indeed, this section will provide the reader with all the data needed to replicate this research. The results are included and discussed in Section 3. Finally, Section 4 contains the main conclusions drawn from this work.

2. Material and methods

The general methodology consists of these main steps:

1. The types of purification station waste were determined.
2. The shells were analysed in terms of their granulometry, specific gravity and composition.
3. Different mixtures were proposed.
4. Mechanical tests were done to characterise compressive strength and superficial absorption (capillarity).
5. In accordance with shell type, proportion and granulometry, a statistical analysis was carried out on compressive strength and water absorption.

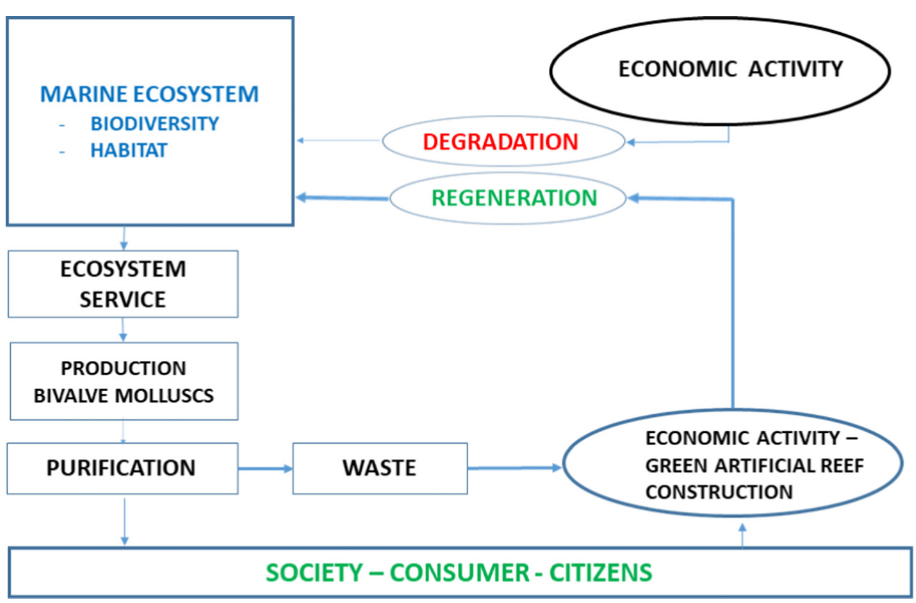

Fig. 1. Circular economy, ecosystem services from shellfish activities. Purification and interaction with ARs towards regenerating marine ecosystems. Source: authors' own.

6. A final decision was made through a multi-criteria analysis, taking into account the environmental relevance of the quantity of waste generated in the purification process, the difficulty of the crushing process, the compressive strength of the concrete after seven and 28 days and superficial absorption.

Further information about several of these stages is provided in the following subsections.

2.1. Analysis of the shells

Due to modifications in the organic and inorganic matrices, the microstructure of bivalve shells varies among the taxonomic groups. (Alonso et al., 2021). Differences in the protein and polysaccharide composition lead to a diversity of organic matrix arrangements (Samata, 1990; Marin and Luquet, 2004). Moreover, the inorganic matrix differs according to the polymorphic phases of $CaCO_3$. These phases are mainly composed of aragonite and calcite, both of which have higher strengths and densities than limestone powder (Kobayashi and Samata, 2006). Even though the chemical composition is varied, they are usually classified as ceramic compounds/organic-mineral (biomineral), 90–99 % of which is $CaCO_3$ and 1 %–10 % of which is proteins and polysaccharides (Kobayashi and Samata, 2006; Barros et al., 2009; Lin and Meyers, 2005; Hamester et al., 2012; Martínez-García et al., 2017).

With the aim of characterising the purification process by-product, the bivalve shells- from scallops, mussels, oysters and clams- were previously washed with water to eliminate high salt concentration (chlorides and sulphates). Subsequently, the shells were heated to 135 °C for 30 min in accordance to regulation 1069/2009 from the European Parliament and Council on health standards related to animal by-products. This treatment eliminated humidity and the possible existence of pathogens (EC, 2009; Martínez-García et al., 2017). A crushing process was then carried out to obtain particle sizes corresponding to fine aggregates (<250 μm).

The granulometry of the crushed particles was determined by means of a Micromeritics laser granulometer with a particle size analysis range of 40 nm to 250 μm. By using the BET method (Brunauer, Emmet, and Teller), it was possible to measure the specific particle surface area from the nitrogen absorption and desorption data obtained with a Micromeritics ASAP 2020 automatic analyser (Brunauer et al., 1938; Michel and Courard, 2014), while specific particle gravity was calculated from the helium pycnometry.

In the final steps of the process, a BRUKER-NONIUS S4 Pioneer wavelength dispersive fluorescence spectrometer was used to analyse the elemental chemical composition through x-ray fluorescence (XRF) of the bivalve waste after it had undergone thermal treatment and the crushing process. Organic matter (OM) and Loss on Ignition (LOI) were determined at 475 °C and 975 °C, respectively, in a muffle furnace. X-ray diffraction of the monochromatic radiation Kα of Cu from powder samples (XRD) made it possible to study the crystallographic phases. Oysters, mussels and clams were analysed through a D5000 Siemens diffractometer; scallops, through a D4 Endeavour Bruker-Nonius diffractometer. The Rietveld refinement method was employed to quantify the phases, and the morphological analysis of the particles was performed by means of a JEOL JSM-6400 scanning electron microscope (SEM).

2.2. Proposed mixtures and mechanical tests

To determine which by-products (shell types) and granulometries were most suitable for their defined uses, the concrete aggregates were partially substituted with crushed shells (0–4 mm and 4–10 mm in size), constituted by aragonite and calcite in variable proportions. Oyster, scallop and clam shells were employed because, as later shown in Section 3, oyster and scallop shells present 98 % calcite and clams shells present 96 % aragonite. Mussel shells were discarded due to their intermediate values: 72.5 % calcite, 26.6 % aragonite, as explained in Section 3.

Once the types of shells had been selected, an optimal dosage was determined according to Carral et al. (2018). A series of white tests (M0), i.e., without recycled materials, was then performed. In the following steps, new dosages were established from the initial optimal dosage according to Carral et al. (2018) and different quantities of fine and medium aggregates were substituted with shells. In this way, the other tests corresponded to concretes with a 20 % substitution of medium aggregates (4–10 mm size), or with a 20 % substitution of fine aggregates by crushed shells (0–4 mm and 4–10 mm), consisting of aragonite and calcite in variable proportions. The remaining base components of concrete were the same for all dosages.

Six different mixtures were proposed. All cases included 300 kg/m^3 of powder binder and 0.57 relation water/cement. The cement was CEM I MR64 CEM I 52,5R – SR5 LAFARGE (EHE-08, 2008), given that this type does not include additives such as fly ash, silica fume or blast furnace slag. Aggregates were partially substituted with inert and crushed shells, a combination of oyster, clam and scallop shells in varying percentages according to Tables 3 and 4. In all cases, the additive MR040 SikaViscocrete20 UNE-EN 934-2 type 3.1-3 was used.

Twelve cubic formworks (10 cm edge) were prepared for each proposed dosage. The moulds had previously been impregnated with a release agent in order to avoid adherence to the mould and also to facilitate the demoulding process after 24 h.

All samples were subjected to the consistency test known as Abrams cone, described in EN 12350-2 (2009). The samples were prepared according to EN 12350-2 (2009), being compacted with a needle vibrator (2 layers - 25 blows per layer), 24 h at the lab at ambient temperature (19–21 °C). The surface was protected with a cover to avoid humidity losses. Demoulding took place after 24 h. Thereafter, the samples were introduced in a water pool at 20 ± 2 °C, where they cured for 7–28 days.

The tests to determine the compressive strength were done according to UNE-EN 12390-3, using three samples for 7 days and another three samples for 28 days. The tests entail compressing the samples until breaking using a compression machine STRENGTH: EE014-01, UNE-EN ISO 7500-1 Class 1, MASS: EE016-03. The regulation applied was UNE-EN 12350-1:06, 12350-2:06, 12390-1:01; 12390-2:01, and 12390-3:03.

As the concrete would be completely immersed in water, it was also necessary to determine the water absorption since this parameter influences the durability of concrete. These tests were performed at low pressure with Karsten pipettes according to the procedure RILEM Test Method number II. The regulation applied was UNE-EN 16302:2016. In order to carry out the tests, the sample surfaces were treated: after 24 h of curing, the samples

Table 3
Substitution percentages of medium aggregates for aragonite (clam) and calcite (oyster and scallop).

Mixture	Aggregates	% Shell				
		Oyster %	Scallop %	Calcite %	Clam %	Aragonite %
M0	51 % granite gravel 6/12 mm + 35 % granite sand +14 % silica sand	0	0	0	0	0
M1	40.8 % granite gravel 6/12 mm + 35 % granite sand +14 % silica sand - 10.2 % calcite	100	0	100	0	0
M2	40.8 % granite gravel 6/12 mm + 35 % granite sand +14 % silica sand +8.95 % calcite – 1.25 % aragonite	75	12.5	87.5	12.5	12.5
M3	40.8 % granite gravel 6/12 mm + 35 % granite sand +14 % silica sand +7.65 % calcite – 2.55 % aragonite	50	25	75	25	25
M4	40.8 % granite gravel 6/12 mm + 35 % granite sand +14 % silica sand +6.35 % calcite – 3.85 % aragonite	25	37.5	62.5	37.5	37.5
M5	40.8 % granite gravel 6/12 mm + 35 % granite sand +14 % silica sand +7.65 % calcite – 2.55 % aragonite	0	50	50	50	50
M11	40.8 % granite gravel 6/12 mm + 35 % granite sand +14 % silica sand +10.2 % aragonite	0	0	0	100	100

Table 4
Substitution percentages of fine aggregates for aragonite (clam) and calcite (oyster and scallop).

Mixture	Aggregates	% Shell				
		Oyster %	Scallop %	Calcite %	Clam %	Aragonite %
M0	51 % granite gravel 6/12 mm + 35 % granite sand + 14 % silica sand	0	0	0	0	0
M6	51 % granite gravel 6/12 mm + 27.6 % granite sand + 11.6 % silica sand + 9.8 % calcite	100	0	100	0	0
M7	51 % granite gravel 6/12 mm + 27.6 % granite sand + 11.6 % silica sand + 8.575 % calcite – 1.225 % aragonite	75	12.5	87.5	12.5	12.5
M8	51 % granite gravel 6/12 mm + 27.6 % granite sand + 11.6 % silica sand + 7.35 % calcite – 2.45 % aragonite	50	25	75	25	25
M9	51 % granite gravel 6/12 mm + 27.6 % granite sand + 11.6 % silica sand + 6.125 % calcite – 3.675 % aragonite	25	37.5	62.5	37.5	37.5
M10	51 % granite gravel 6/12 mm + 27.6 % granite sand + 11.6 % silica sand + 4.9 % calcite – 4.9 % aragonite	0	50	50	50	50
M12	51 % granite gravel 6/12 mm + 27.6 % granite sand + 11.6 % silica sand + 9.8 % aragonite	0	0	0	100	100

were demoulded and the top surfaces were roughened. These were used as test surfaces. After 28 days of curing, the samples were dried for 72 h in a thermos-ventilated oven at 60 ± 2 °C and tempered to 23 ± 2 °C for testing.

2.3. Statistical analysis

A descriptive statistical analysis was performed on the properties that characterise the different concrete samples studied. Moreover, the relationship was modelled between the different features that would ultimately define how these concretes were to be used. The variables critical to quality (CTQ) for the concrete were identified. As the first step in the statistical analysis, the position, dispersion and relation of these variables within the design parameters were studied through an exploratory analysis, developing the so-called graphical ANOVA. Moreover, multi-factor ANOVA techniques, such as the F test, were applied. The relation of the CTQ variables was studied with respect to the quantity of calcite, and amount of oyster, scallop, and clam shells, from an inferential perspective by applying multivariate regression models. Furthermore, the relation between CTQ variables and design parameters were also modelled by the estimation of multivariate regression models.

In order to identify the significant dependences and their types, linear or nonlinear, Generalised Additive Models (GAM) were fitted (Janeiro-Arocas et al., 2016; Robles-Bykbaev et al., 2018; Robles-Bykbaev et al., 2019). These were semiparametric multivariate regression models that made it possible to include both the linear and smooth (nonparametric) effects of the covariates on the response in the model's expression. They could be used prior to applying parametric models in order to identify if the effects of covariates were linear or nonlinear.

2.4. Multi-criteria analysis

Several, usually conflicting, criteria or indicators are considered when carrying out most of the real decision-making processes. In this sense, there is usually no alternative with the best performance in each attribute analysed. At this point, a methodology or tool is needed to integrate the results of the different criteria for each alternative into a single value, facilitating the selection process. These techniques are the so-called multi-criteria decision-making methods (MCDM).

MCDM can be classified into two main groups: i) multiple objective decision-making (MODM) and ii) multiple attribute decision-making (MADM) methods (Hwang and Yoon, 1981). MADM methods deal with the selection of the best alternative from a set of previously defined and known options. Therefore, these methods were chosen for this study.

MADM methods can also be classified into different sub-groups. Although there is no single way of classifying these techniques, one of the most common is proposed by Penadés-Plà et al. (2016). According to the authors, the following sub-groups can be distinguished: i) direct scoring, ii) pairwise comparison, iii) outranking, iv) distance-based, and v) value methods. Within each one of these five sub-classifications, there are multiple techniques with a range of nuances.

As each MADM method has its own particular approach, it is usually advisable to employ at least two different procedures. If the definition and assessment of the different criteria is properly reasoned, the results of different methods should be similar. This does not mean that they must be exactly the same. However, there should be no remarkable differences between the rankings. Therefore, the use of more than one MADM technique to solve the same problem serves to measure the robustness and consistency of the results obtained. This is the main reason why two different techniques were applied in this study. Another reason is that there is no perfect MADM method; they all have weaknesses and strengths. In particular, for this study, simple additive weighting (SAW) and the VlseKriterijumska Optimizacija I Kompromisno Resenje (VIKOR) techniques were used.

SAW is a direct scoring technique developed by Churchman and Ackoff (1954). Due to its simplicity, it is one of the most widely used. The V_i parameter is employed to assess the performance of each alternative *i*. It varies between 0 and 1, the worst and best possible results, respectively. More information about the SAW calculation process is provided in Appendix A.

On the other hand, VIKOR is a distance-based method defined by Opricovic (1998). The interpretation of the results provided by VIKOR is not as simple as that of SAW, since the different alternatives can be classified according to three parameters (R_i, S_i and Q_i, Appendix A). In all cases, the lower the value, the better the performance of the alternative. Consequently, VIKOR allows the user to create three different rankings and the position that certain alternative occupies in each ranking does not have to be the same. However, this problem is partially overcome by the possibility of choosing the compromise solution. Appendix A provides the reader with further information on VIKOR.

The indicators included in the multi-criteria analysis of the different concrete mixtures are shown in Table 5. As can be seen, two new criteria were considered in comparison with the statistical analysis (Sections 2.3 and 3). They were: i) the difficulty of the crushing process and ii) the environmental relevance of the waste generated. In both cases, a scale of points was defined.

Table 5
Criteria considered in the multi-criteria analysis, including the measurement units, trends and weights. Source: authors' own.

Criterion	Units of measurement	Trend	Weight (w_j)
Compressive strength (7 days)	Units (MPa)	Increasing (maximise)	1/9
Compressive strength (28 days)	Units (MPa)	Increasing (maximise)	2/9
Water absorption by capillarity	ml/cm^2	Decreasing (minimise)	2/9
Difficulty of the crushing process	Points	Decreasing (minimise)	1/18
Environmental relevance of waste	Points	Increasing (maximise)	7/18

However, the difficulty of the crushing process was a decreasing parameter, while the environmental relevance of the waste generated was an increasing indicator.

In terms of the difficulty of the crushing process, the score of each mixture was obtained by using Eq. (1).

$$Score\ crushing\ process = 1.5 \cdot P_{oyster} + 1.25 \cdot P_{scallop} + 1 \cdot P_{clam} \quad (1)$$

where, P_{oyster}, $P_{scallop}$ and P_{clam} were the percentages of oyster, scallop and clam used in each mixture (Tables 3 and 4). Each percentage was multiplied by a factor reflecting the difficulty of crushing each type of shell. In this regard, the clam shell was the easiest to crush (1), followed by scallop (1.25) and oyster (1.5). Those values were defined based on the personal experience of the authors, who had to crush the shells by various means. Similarly, the score that each mixture adopts in terms of environmental relevance of the waste generated was estimated through Eq. (2).

$$Score\ environmental\ relevance = 1 \cdot P_{oyster} + 1.5 \cdot P_{scallop} + 1 \cdot P_{clam} \quad (2)$$

The Spanish regulations do not distinguish between the disposal of 1 tonne of oyster shell, scallop shell or clam shells. Nevertheless, in the particular case of Galicia, the reutilisation of the scallop shell has to be prioritised: oyster and clam shells are processed at destination, while half of the scallop shells are processed at origin and the other half at destination. This is the reason why a factor of 1.5 was defined for the scallop shell, since it represents an added problem to the shellfish industry.

Although SAW and VIKOR are different methods, both entail defining weights (w_j) for the indicators considered in the analysis. Consequently, certain points require clarification. Incorporating shells into the manufacture of artificial reefs contributes to both the circular economy and sustainability. Consequently, the highest relative importance (7/18) was assigned to the environmental indicator. In contrast, the compressive strength at 7 days is not a definitive parameter; its relevance is due to the need of reaching a minimum value that makes the demoulding process possible. Once this threshold is reached, this mechanical property is no longer of interest. By contrast, the compressive strength after 28 days and the water absorption are two definitive mechanical properties that affect the final performance of the reef, as well as its durability. Therefore, a weight of 1/9 was defined for the compressive strength at 7 days, while a value of 2/9 was established for the other two mechanical properties. Finally, the lowest weight was defined for the difficulty of the crushing process, as it

Table 7
Granulometric particle distribution after the crushing process (% vol).

	Scallop (flat)	Scallop (concave)	Mussel	Oyster	Clam
250 μm–125 μm	1.1	1.2	0.2	0.0	0.0
125 μm–63 μm	13.2	12.0	13.8	7.2	11.2
63 μm–45 μm	12.0	12.2	14.0	9.9	13.7
45 μm–20 μm	18.7	28.7	23.1	24.4	29.1
20 μm–10 μm	8.5	13.6	9.6	13.1	13.4
10 μm–5 μm	5.6	6.7	6.4	8.2	6.3
5 μm–2 μm	10.8	6.6	10.9	10.8	5.1
<2 μm	30.1	19.0	22.0	26.4	21.2
D90 (μm)	68.9	68.9	68.9	54.7	61.4
D50 (μm)	12.3	21.8	20.6	12.3	21.8
D10 (μm)	0.16	0.31	0.33	0.31	0.21
SPAN = (D90-D10)/D50	5.59	3.14	3.33	4.42	2.81

Table 6
Values (x_{ij}) that each mixture adopts for the indicators. Source: authors' own.

Mixture	Compressive strength (7 days)	Compressive strength (28 days)	Water absorption	Difficulty of the crushing process	Environmental relevance of wastes
M0 (sample 1)	40.2	45.5	0.08	0	0
M0 (sample 2)	40	46	0.08	0	0
M0 (sample 3)	40.3	45.7	0.08	0	0
M1 (sample 1)	34.3	39.4	0.08	150	100
M1 (sample 2)	34.7	39.8	0.08	150	100
M1 (sample 3)	34.4	40.8	0.08	150	100
M2 (sample 1)	33.8	37.9	0.08	140.625	106.25
M2 (sample 2)	32.6	40.5	0.08	140.625	106.25
M2 (sample 3)	34.1	39.9	0.08	140.625	106.25
M3 (sample 1)	32.8	38.2	0.14	131.25	112.5
M3 (sample 2)	32.7	37.4	0.14	131.25	112.5
M3 (sample 3)	31.7	38	0.14	131.25	112.5
M4 (sample 1)	31	37.8	0.16	121.875	118.75
M4 (sample 2)	30.9	36.9	0.16	121.875	118.75
M4 (sample 3)	32	37.1	0.16	121.875	118.75
M5 (sample 1)	35.3	41	0.12	112.5	125
M5 (sample 2)	34.4	40.9	0.12	112.5	125
M5 (sample 3)	33.8	42.1	0.12	112.5	125
M6 (sample 1)	30.9	35.8	0.16	150	100
M6 (sample 2)	29.5	36.4	0.16	150	100
M6 (sample 3)	29.6	36.9	0.16	150	100
M7 (sample 1)	26.9	34.9	0.16	140.625	106.25
M7 (sample 2)	30	31.7	0.16	140.625	106.25
M7 (sample 3)	27.4	33.6	0.16	140.625	106.25
M8 (sample 1)	26.6	34.2	0.16	131.25	112.5
M8 (sample 2)	28.2	32.9	0.16	131.25	112.5
M8 (sample 3)	28.1	33.7	0.16	131.25	112.5
M9 (sample 1)	29.1	32.5	0.16	121.875	118.75
M9 (sample 2)	28.6	32.9	0.16	121.875	118.75
M9 (sample 3)	27.8	32.9	0.16	121.875	118.75
M10 (sample 1)	27	33.5	0.16	112.5	125
M10 (sample 2)	29.2	31.8	0.16	112.5	125
M10 (sample 3)	28.4	33.2	0.16	112.5	125
M11 (sample 1)	29.2	35.9	0.12	100	100
M11 (sample 2)	29.6	35.9	0.12	100	100
M11 (sample 3)	27.4	35.2	0.12	100	100
M12 (sample 1)	33	39.6	0.16	100	100
M12 (sample 2)	32.1	39.7	0.16	100	100
M12 (sample 3)	32.7	39.5	0.16	100	100

Table 8
Specific surface obtained through absorption techniques using Brunauer, Emmett and Teller (BET) methods and specific gravity (d).

Sample	BET (m^2/g)	d (g/cm^3)
Scallop-HM_flat	5.7	2.70
Scallop-HM_concave	7.1	2.70
Mussel-HM	3.7	2.70
Oyster-HM	4.0	2.68
Clam-HM	5,4	2,84

Table 9
Composition of shells characterized by x-ray fluorescence (XRF).

	Oyster	Clam	Mussel	Concave scallop Fcóncava	Flat scallop
CaO	53.9	53.8	53.8	54.7	54.9
Ca as $CaCO_3$	96,25	96.07	96.07	97.68	98.04
SiO_2	0.85	0.35	0.16	0.46	0.29
Na_2O	0.59	0.51	0.33	0.28	0.29
SO_3	0.39	0.19	0.24	0.63	0.65
MgO	0.25	0.074	0.22	0.23	0.17
SrO	0.11	0.19	0.14	0.13	0.14
Cl	0.099	0.022	0.20	= =	= =
Al_2O_3	0.097	0.016	0.009	0.062	0.044
P_2O_5	0.090	0.053	0.042	0.089	0.093
K_2O	0.037	0.016	0.007	0.017	0.013
TiO_2	0.016	= =	= =	= =	= =
Fe_2O_3	0.016	= =	= =	0.050	= =
CuO	0.009	0.009	0.009	0.010	0.009
ZnO	0.005	0.006	0.007	0.007	0.007
ZrO_2	0.005	0.007	0.005	0.005	0.005
Br	= =	= =	0.008	= =	= =
MO(*)	2.1	2.5	3.1	1.8	1.7
LOI	43.5	44.7	45.0	43.3	43.4

could be done automatically with the corresponding equipment. In Table 6, the reader can find the values (x_{ij}, Appendix A) that each mixture adopts for the indicators (x_{ij}) measured in the units of Table 5.

3. Results and discussion

Given that this study is ground-breaking on several fronts, it is difficult to compare its results with those from existing studies. In particular, as indicated in Section 1, this is the first time that bivalve purification waste has been used for proposing different concrete mixtures combining several shell types. This is also the first time that these dosages have been subjected to statistical and multi-criteria analyses to determine the best alternative for manufacturing green artificial reefs. This section is divided into three subsections. The results derived from the shell analysis and mechanical tests are included in Section 3.1, as they are closely related. The statistical and multi-criteria results can be found in Sections 3.2 and 3.3, respectively.

3.1. Results of the shell analysis and mechanical tests

Table 7 contains the granulometric distribution of the particles after the crushing process for the different types of shells had been carried out. The specific surface and specific gravity are included in Table 8. The higher specific gravity, 2.84 g/cm^3, corresponds to the clams, while the other molluscs present similar values between 2.68 and 2.70 g/cm^3.

Table 9 shows the chemical composition obtained through x-ray fluorescence (XRF) of the bivalve waste once the thermal treatment and crushing process had been performed. As can be seen, the main metallic component of the shell is calcium and, in particular, calcium carbonate. Small quantities of silicon oxide, sodium oxide, sulphur oxide (VI), magnesium oxide and strontium oxide are also present. The chloride content is relatively high in mussels in comparison with oysters and clams. Scallops did not reveal any chlorine content. The lower percentages of organic matter were detected in scallops (1.7 % wt in the flat shells and 1.8 % wt in the concave ones), while the higher percentages corresponded to mussels (3.1 % wt). This organic part mainly comprises proteins, peptides and lipids.

It is important to differentiate between the mechanical properties of shell aggregates and the global properties they can provide to the concrete. As isolated materials, the mechanical properties are better than those corresponding to inorganic calcium carbonate, both as aragonite and/or calcite. The reason for this lies in the presence of inorganic matter that provides higher tensile and compressive strengths, especially in the pearly zone. In any case, the mechanical strength of the shells depends on environmental conditions during their formation. In this way, for example, Lassoued et al. (2021) reported a diminution on the mechanical strength of mussel shells under moderately or highly acidified seawater.

Very high temperatures used during the thermal treatment may cause the organic matter to degrade. They may also lead to a reduction in the

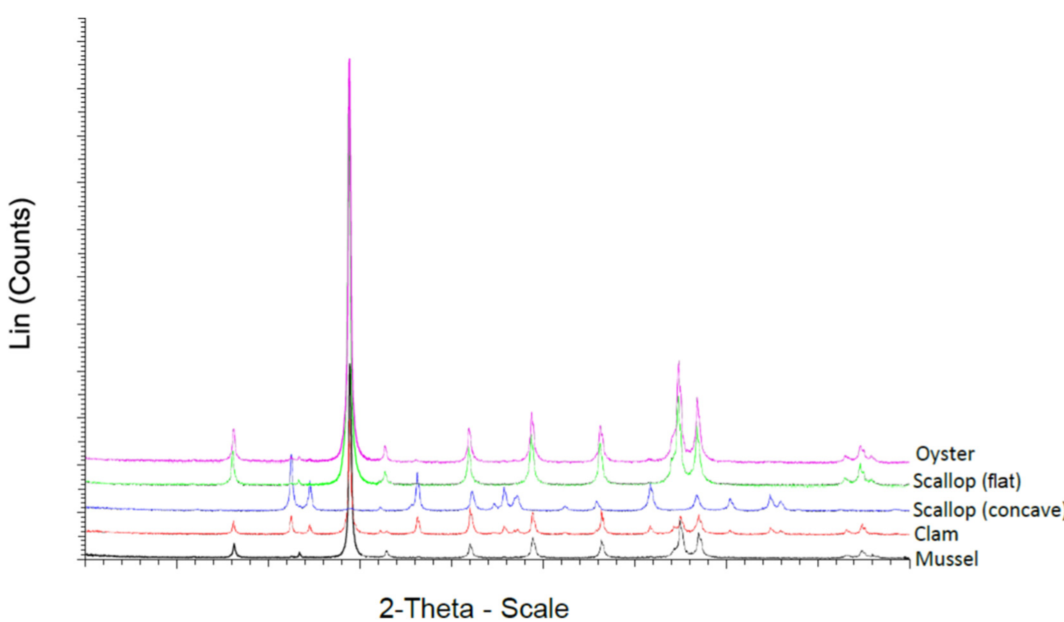

Fig. 2. X-ray diffraction of the samples. Oysters, mussels and clams were analysed through a D5000 Siemens diffractometer, while scallops were analysed through a D4 Endeavour Bruker-Nonius diffractometer. The main peaks are more intense on the scallop diffractograms because the D5000 runs at 30 kV and 40 mA, while the D4 at 40 kV and 40 mA.

Table 10
Weight percentage of the main crystalline phases characterised by x-ray diffraction.

Sample	Calcite	Aragonite	Quartz
Oyster	**97.8**	1.1	1.1
Mussel	72.5	26.6	0.9
Clam	1.9	**96.3**	1.8
Scallop (flat)	**97.4**	2.2	0.4
Scallop (concave)	**99.3**	0.3	0.4

Bold data indicates the main crystalline phase.

mechanical strength of the arid. Nevertheless, the higher hardness of aragonite (3.5–4 according to Mohs scale) in comparison with that of calcite (3.0 according to Mohs scale) can improve the erosive degradation strength in concretes where the former is employed as an aggregate.

The presence of aragonite in bivalve shells is related to the processes of nacre formation inside the shells, blended with coquioline, while calcite constitutes the intermediate shell layer, together with aragonite. Mainly composed of organic compounds, the external layer quickly decomposes after the mollusc die. Under normal conditions, calcite is thermodynamically more stable than aragonite. For this reason, high temperatures and the course of time favour the presence of calcite. The relation between calcite and aragonite may be altered by environment conditions. In this way, Telesca et al. (2019) determined that the sea regions in which salinity and temperature are low boast a higher quantity of calcite in mussel shells. On the other hand, the quantity of aragonite is higher in warm and high salinity seas.

Fig. 2 illustrates the x-ray diffraction (XRD) results corresponding to the five types of shells analysed, while Table 10 shows a quantification of the main crystalline phases detected. The main inorganic compound is calcium carbonate, which forms two allotropic varieties: calcite and aragonite (Harper, 2000; Yoon et al., 2003). As can be seen, a high variation in the proportions of calcite and aragonite can be found, depending on mollusc type. In this way, oysters and both scallop shells (flat and concave) present almost all calcium carbonate as calcite (96.3 %, 99.3 % and 97.4 % wt of the total $CaCO_3$, respectively), while clams present it as aragonite (96.3 % wt of the total $CaCO_3$). These results agree with those obtained by other researchers. For instance, He et al. (2015) reported that nearly 100 % of the inorganic phase of scallop shells is calcite. In mussels, most CaCO3 is present as calcite (72.5 % wt) with a relatively significant aragonite content (26.6 %).

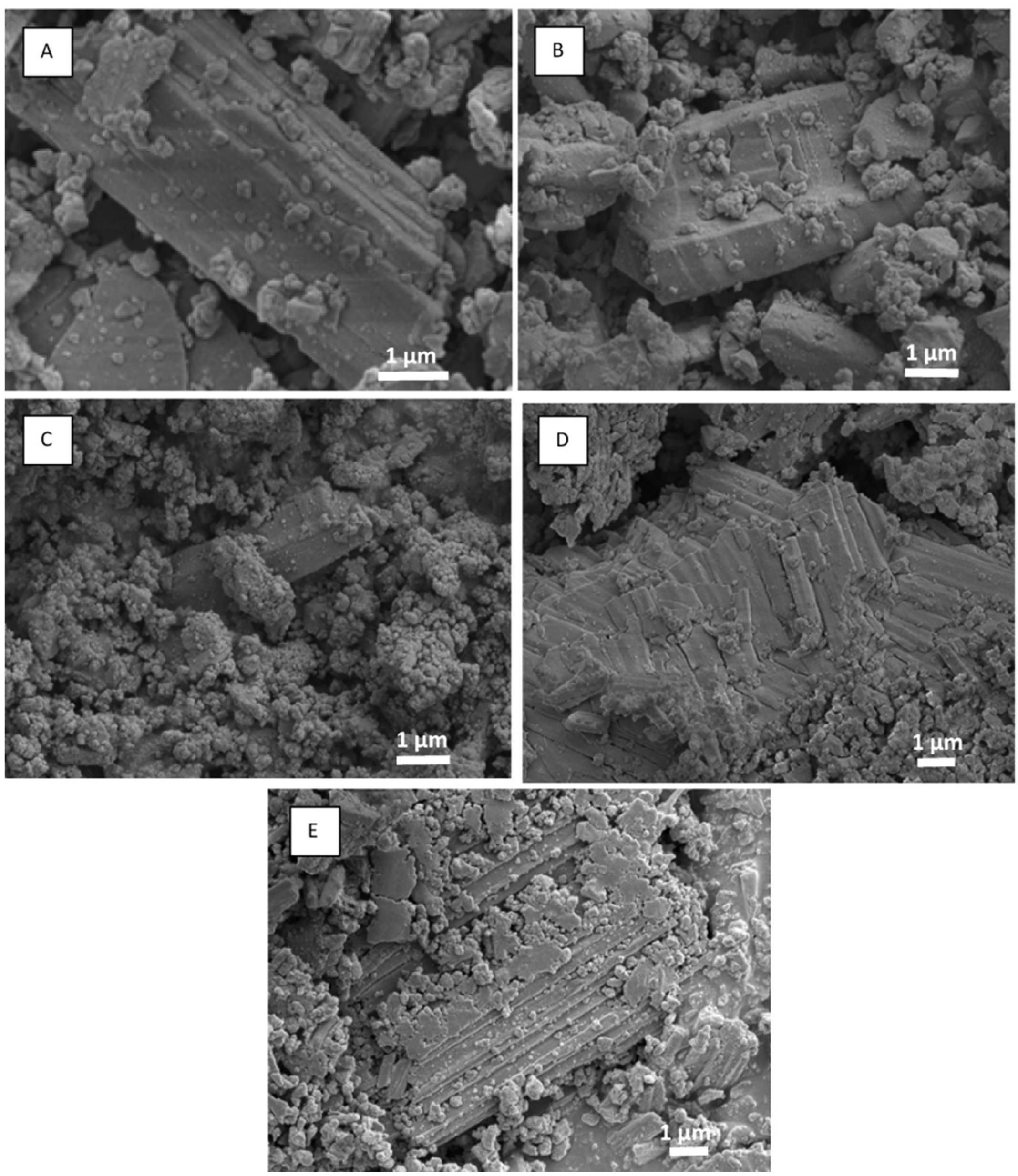

Fig. 3. SEM images with oyster (A), mussel (B), clam (C), flat scallop (D) and concave scallop (E) samples.

Table 11
Results of the mechanical tests corresponding to the substitution of medium aggregates. Compressive strength and water absorption by capillarity and in mass.
(1) – absorption – penetration of water without pressure (ml/cm^2) after 60 min.
NOTE. The substitution of aggregates for shells confers poor docility to the mixture.

Sample	M0 - white	M1	M2	M3	M4	M5	M11
Cement	MR64 CEM I 52.5R - SR5 LAFARGE						
Cement content (kg/m$_3$)	300						
Water/cement relation	0.57						
Apparent density	2320/2330/2340	2250/2250/2260	2280/2270/2220	2230/2220/2220	2230/2240/2260	2280/2280/2290	2280/2290/2280
Compressive strength							
Cubic breaking load, 7 days (kN)	401/400/403	343/347/344	337/326/341	328/327/316	310/309/320	353/343/337	292/296/273
Compressive strength, 7 days	40.2/40.0/40.3	34.3/34.7/34.4	33.8/32.6/34.1	32.8/32.7/31.7	31.0/30.9/32	35.3/34.4/33.8	29.2/29.6/27.4
Cubic breaking load, 28 days (kN)	455/459/456	393/398/408	379/404/399	381/374/380	377/369/371	410/408/421	359/358/351
Compressive strength, 28 days	45.5/46/45.7	39.4/39.8/40.8	37.9/40.5/39.9	38.2/37.4/38	37.8/36.9/37.1	41.0/40.9/42.1	35.9/35.9/35.2
Water absorption by capillarity and in mass (1)	0.08	0.08	0.08	0.14	0.16	0.12	0.12
Allotropic variety predominant on shell mixture		Calcite					Aragonite

The global mechanical properties of concretes with shell aggregates are inferior to those of conventional concrete due to particle morphology, higher specific surface, higher water absorption and the presence of organic matter. It must be taken into account that, when the specific surface is incremented, the volume of cement and water and the relation between water and cement must be higher in order to obtain a suitable degree of docility in the concrete. As shown in Table 8, the higher specific gravity corresponds to scallop and clam samples. This value depends on both the granulometric distribution of the aggregates (see Table 7) and the morphology of the individual particles. Regarding the latter, the SEM images illustrated in Fig. 3 show that both oyster and scallop particles, where the calcium carbonate remains as a calcite type, present a layered laminar structure. Nevertheless, this structure does not appear on mussels or clams. It is worth mentioning that both a lower specific surface in the arid and the presence of organic matter in the shells may lead to a lower adherence between the cement and aggregates, which increments the porosity of the concrete (Martínez-García et al., 2017).

The presence of one specific polymorphic variety of calcium carbonate or another has a substantial impact on the mechanical properties of the concretes. Thus, Li et al. (2019) verified that the compressive and bending strengths of concretes with inorganic $CaCO_3$ are lower when these include calcite than when they contain aragonite whiskers due to a high formation of hydration products on calcite. Another aspect to take into account is the higher seawater solubility of aragonite (approximately 50 % higher than calcite) (Morse et al., 1980), resulting in a higher porosity in concretes and lower adherence of cement to aggregates.

The incorporation of calcite and aragonite shells contribute to creating a dense calcium carbonate protective layer along the concrete's surface. This layer provides protection against chemical attacks from seawater (Camba et al., 2021). An important conclusion that can be extracted from the results is that the water absorption is lower when the medium arid is substituted, and when calcite predominates over aragonite. When medium aggregates are substituted and calcite prevails over aragonite, the strength is increased due to a filling action. On the other hand, the substitution of fine aggregates increments the strength when aragonite (clam) prevails (Tables 11 and 12).

3.2. Results of the statistical analysis

The statistical techniques applied in this work focus on the possible relationship between critical variables for concrete quality (compressive strength and water-absorbed volume) and the design variables, including size of the added bivalve shell aggregates, the amount of calcite from the addition of shells and the amount of shells according to each type of bivalve. The results obtained by using this application are intended to support decision making in the design and construction of artificial reefs. For these tasks, both descriptive statistical techniques (graphical ANOVA) and regression modelling were employed.

In order to show the results in a more illustrative way, the M0-M12 formulations have been relabelled attending to their composition, from T0 to T6. Thus, where T0 is the control formulation, M0, T1 corresponds to the M1 (fine aggregates) and M6 (medium aggregates) samples, the T2 level corresponds to the M2 and M7, T3 corresponds to M3 and M8, T4 to M4 and M9, T5 to M5 and M10, and T6 to M11 and M12.

Fig. 4 shows the effect of variations in the amount of calcite, oyster, scallop and clam shells have on the compressive strength of the resulting concrete. Likewise, the effect of size of these aggregates is shown, in addition to the concrete curing time or age. Fig. 4a shows a clear increase in compressive strength, for almost all concrete formulations, when aggregate size goes up (from fine to medium size). The exception is the formulation labelled T6 (M6 and M12), which contains no calcite, only aragonite

Table 12
Results of the mechanical tests corresponding to the substitution of fine aggregates. Compressive strength and water absorption by capillarity and in mass.
(1) In this case, the shells are finer, an aspect which favours the substitution of sand instead of gravel (in contrast with the previous case).
Absorption – penetration of water without pressure (ml/cm^2) after 60 min.

Sample	M0 - white	M6	M7	M8	M9	M10	M12
Cement	MR64 CEM I 52.5R - SR5 LAFARGE (1)						
Cement content (kg/m^3)	300						
Water/cement relation	0.57						
Apparent density	2320/2330/2340						2310/2320/2300
Compressive strength							
Cubic breaking load, 7 days (kN)	401/400/403	308/295/296	269/299/274	266/282/281	290/286/277	270/291/284	330/320/327
Compressive strength, 7 days	40.2/40.0/40.3	30.9/29.5/29.6	26.9/30.0/27.4	26.6/28.2/28.1	29.1/28.6/27.8	27.0/29.2/28.4	33.0/32.1/32.7
Cubic breaking load, 28 days (kN)	455/459/456	358/364/369	349/316/335	342/329/336	324/329/329	334/318/332	396/396/395
Compressive strength, 28 days	45.5/46/45.7	35.8/36.4/36.9	34.9/31.7/33.6	34.2/32.9/33.7	32.5/32.9/32.9	33.5/31.8/33.2	39.6/39.7/39.5
Water absorption by capillarity and in mass	0.08	0.16	0.16	0.16	0.16	0.16	0.16
Allotropic variety predominant on shell mixture		Calcite					Aragonite

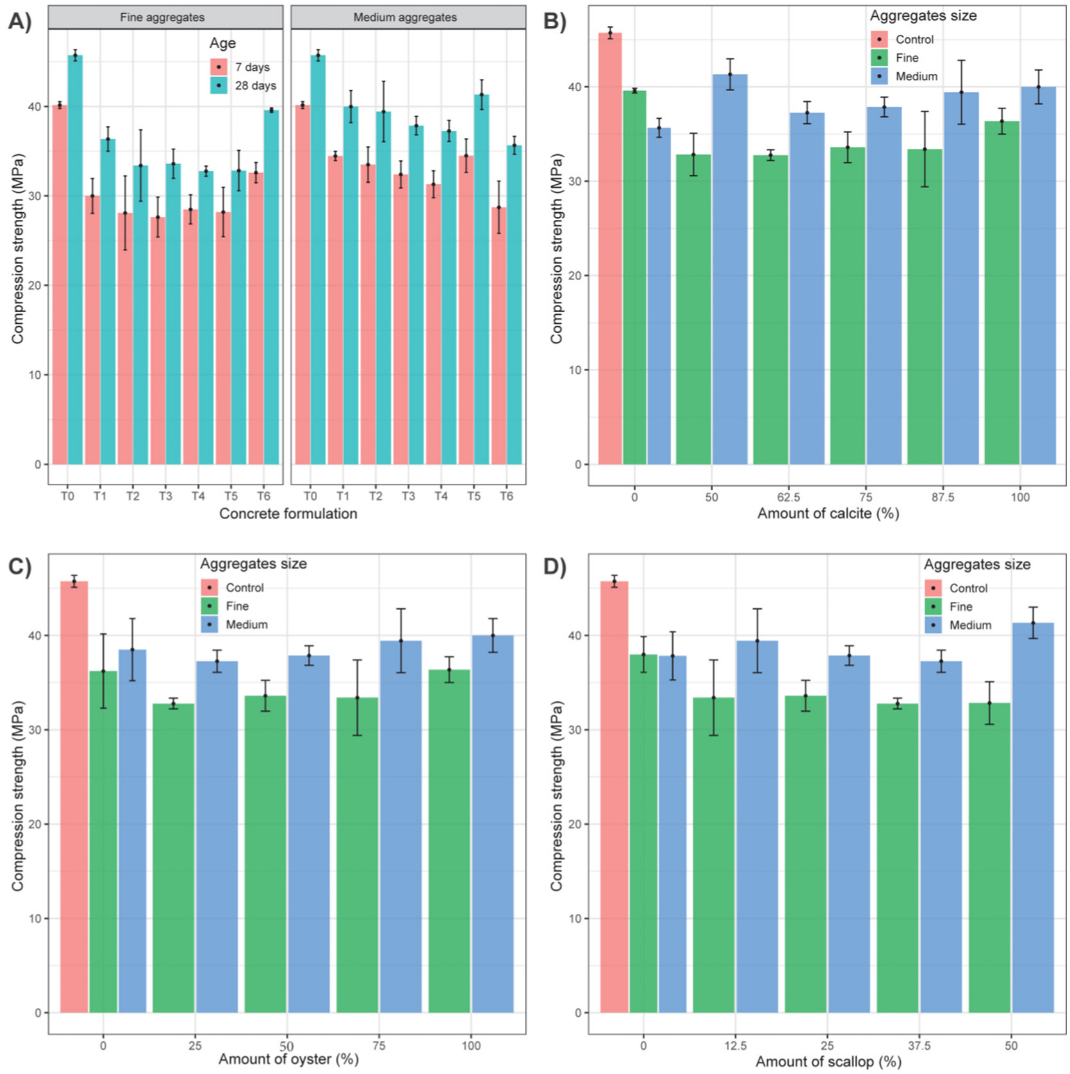

Fig. 4. Effects of the concrete formulation, aggregates size and calcite, oyster, and scallop percentage on the concrete compression strength. 95 % confidence intervals for the mean strength, for each combination of factors, are included.

belonging to clam shells. Here a decrease in strength can be detected from fine to medium aggregates. On the other hand, as already expected, a significant increase in compressive strength is also observed with increasing concrete age (from 7 to 28 days).

The effect of the increase on calcite addition (measured as calcite proportion, %) is not so intuitively and clearly observed. Of course, an increase in compression strength, as the calcite percentage goes up, can be seen in Fig. 4b. Nevertheless, these changes are slight if compared with the width of 95 % confidence intervals for the mean strength. In fact, the intervals tend to be overlapped. The observed differences could therefore not be significant. The concrete compressive strength also seems to slightly increase when the percentage of oyster shell goes up, although the overlapping of the 95 % confidence intervals for the mean strength also tends to overlap.

When the amount of scallop shell is raised, the strength tends to slightly decrease or remain constant (taking into account the overlapping intervals). In any case, this trend is broken when a quantity of 50 % of scallop shells is added. In fact, the sudden rise in compressive strength when an amount of 50 % of scallop is added could be also related to the size of the aggregates, since a controlled size is harder to obtain due to the high width and other features of the scallop shell. From the latter results, it could be inferred that the rise in the strength is higher if the calcite comes from oyster, as opposed to scallop shells.

In order to asses if these design factors have a significant effect on the compressive strength of the concrete (remaining constant the age of the concrete at 60 days), ANOVA for multiple factors was applied, specifically the F test. Consequently, the effects of aggregate size (p-value $= 0.00218 < 0.05$), oyster percent (p-value $= 0.001439 < 0.05$) and calcite proportion (p-value $= 0.000552 < 0.05$) on compressive strength are shown to be significantly different from zero.

If only the value of the concrete's compressive strength is considered, it can be seen that this value decreases whenever part of the aggregate is replaced with mollusc shells. In any case, the differences are very small if the aggregate is replaced with 87.5–100 % calcite coming from medium-sized aggregates, mostly from oyster shells, specifically the M1 (T1 with medium-sized aggregates) and M2 (T2 with medium-sized aggregates). If fine aggregates are used, the formulation M12 (T6 with fine aggregates), only the one with 100 % aragonite, provides the highest strength.

Moreover, Fig. 5 shows descriptive information regarding the influence of design parameters (size of aggregates and proportion of calcite, oyster, scallop, aragonite and clam shells) on the concrete water absorption. In fact, the volume of water absorption depending on the mean values of the design parameters is presented. Specifically, Fig. 5a shows the concrete water absorption volume depending on the formulation, aggregate size and the time of the lab experiment (called Time).

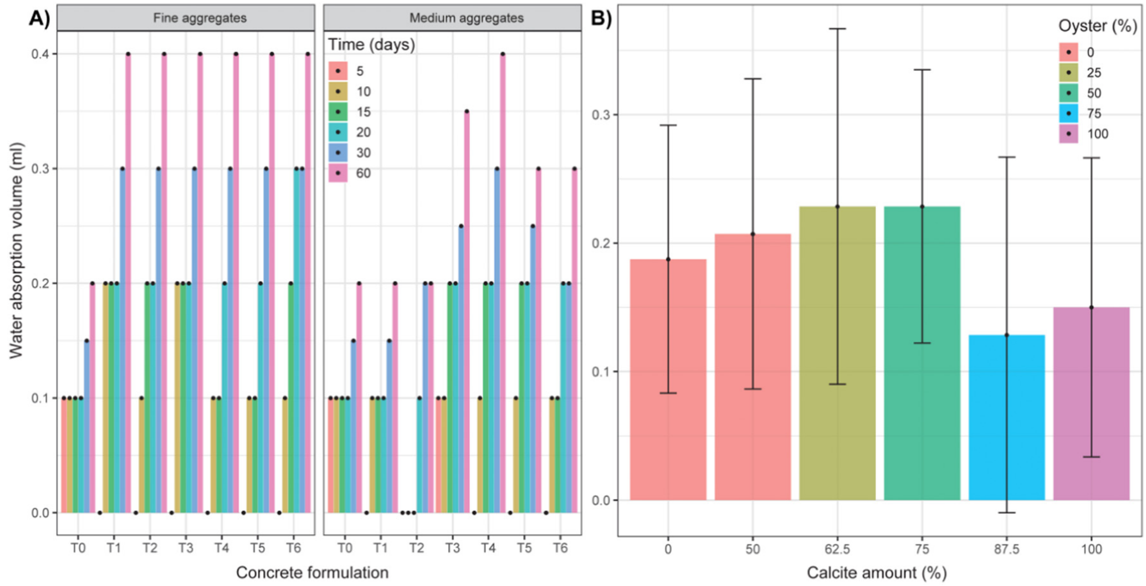

Fig. 5. Panel A shows the volume of water absorption in the concretes depending on the formulation, aggregate size and the time of the water absorption experiment. Panel B shows the compressive strength depending on the percentages of calcite and oyster. 95 % confidence intervals for the mean value are also included.

On the other hand, Fig. 5b accounts for the volume of water absorbed, depending on the percentages of calcite and oyster. In order to facilitate the comparison, 95 % confidence intervals for the mean values are also included in Fig. 5b. As might be expected, the lowest values of water volume absorbed correspond to concrete without mollusc shell substitution (Fig. 5a). However, similarly low absorption values are also obtained for T1 and T2 formulations with a medium aggregate size (i.e., M1 and M2). Even the T2 formulation (M2) appears to absorb water more slowly than the control samples (T0 or M0) at short exposure times. Consequently, as pointed out in Fig. 5b, lower water absorption values are reached when a very high proportion of calcite (≥87.5 %) is included in the formulations, so that the oyster aggregates (≥75 %) prevail over scallop aggregates.

In summary, the formulations that provide the best balance between a relatively high compressive strength and low water absorption (comparable with the control formulation) are the ones denominated M1 and M2. Therefore, design parameters will be sought to correspond to a medium aggregate size, a high calcite addition (>87.5 %) and a calcite that comes mostly from oyster shells (>75 %). In any case, if a multifactor ANOVA model is estimated and the F-test is calculated, it is observed that the linear effects of the change on the proportion of calcite (p-value = 0.38558) and oyster (p-value = 0.21271) are not significantly different from zero (on the contrary, that of aggregate size is significant, p-value = 0.009). It would be necessary to study whether these effects are nonlinear. This can be done by applying nonparametric regression models, as shown below.

These relations between CTQ variables and design parameters can be modelled by estimating multivariate regression models. In order to identify the significant dependences and their type, linear or nonlinear, Generalised Additive Models (GAM) have been fitted (Janeiro-Arocas et al., 2016; Robles-Bykbaev et al., 2018; Robles-Bykbaev et al., 2019). They are semiparametric multivariate regression models that make it possible to include in the expression of the model both linear and smooth (nonparametric) effects of the covariates on the response. They can be used prior to the application of parametric models in order to identify if the effects of covariates are linear or nonlinear. When the results of the descriptive analysis are considered, the compression strength seems to depend on concrete age, aggregates size, calcite percentage and whether this calcite comes from oyster or scallop.

Thus, a GAM model (assuming Gaussian response) has been fitted to explain the compressive strength as a function of the concrete age, the shell aggregate size and percentage of oyster ($R^2_{Adjusted} = 82.4\%$). These variables have been selected following a statistical significance analysis (p-values of t and F statistics <0.05). Fig. 7a–c show the effect of the covariates on the concrete compressive strength. The effects of concrete age and aggregate size are linear, whereas those of oyster percentage are a polynomial type (parabolic). In fact, when 0 % of oyster is added, this is related to the control formulation (M0), defined by a relatively high strength. Moreover, when low proportions of oyster are added, the strength also tends to be low. In contrast, the strength increases in a nonlinear way when the amount of oyster shell is continuously raised. It is important to note that this model is applicable under the current experimental scheme: that is, when a 0 % calcite level is defined by the reference concrete sample (without added shells). Taking into account these results, the following multivariate linear regression model is proposed to explain the concrete compressive strength:

$$\begin{aligned} Strength &= 38.09 - 10.64 \cdot Aggregates[Fine] - 7.066 \cdot Aggregates[Medium] \\ &\quad + 0.2775 \cdot Age - 0.06946 \cdot Oyster + 0.00082 \cdot Oyster^2; R^2 \\ &= 83.6\%. \end{aligned} \tag{3}$$

The effects of the covariates on the compression strength are observed in Fig. 7a–c. When the concrete age goes up, the strength increases in a linear way. Regarding the effects of the aggregates, as pointed out in the descriptive analysis, if they are fine, the compressive strength is induced to be 10.64 MPa lower. If a medium aggregate is added, the strength tends to drop significantly less, by 7.066 MPa on average. Fig. 7b shows the mean effects of aggregate size, their 95 % confidence interval and the partial residuals of the model for each observation (pink dots). Moreover, a polynomial of degree 2 has been fitted to reproduce the parabolic (opened upwards) effect of the oyster percentage (Fig. 7c). This model explains the 83.6 % of the overall variability in the compressive strength. Of the overall explained variability, age explains 46.7 %, whereas aggregates size explains 46.2 % and the oyster percentage (as a polynomial function), the remaining 7.1 % (see Fig. 7d). Therefore, although it is not the most influential design parameter, the amount of calcite from oyster shells significantly influences the compressive strength of concrete (p-value of F statistic = 0.00711 < 0.05).

Similarly, a GAM model has also been fitted to explain the volume of water absorbed (in the framework of the water absorption experimental design described in previous sections), to identify which covariate effects are actually significantly different from zero, and to identify whether they are linear or nonlinear. Fig. 6e–g show the significant effects of aggregates size, time of exposition to water and percentage of oyster shells, given a GAM model defined by a $R^2_{Adjusted} = 80.7\%$. The effect of time seems to be logarithmic (Fig. 6e), whereas the effect of the oyster percentage is also a nonlinear, polynomial type (Fig. 6g), i.e. the minima of water absorption are reached for the control sample (M0) or for formulations with a very

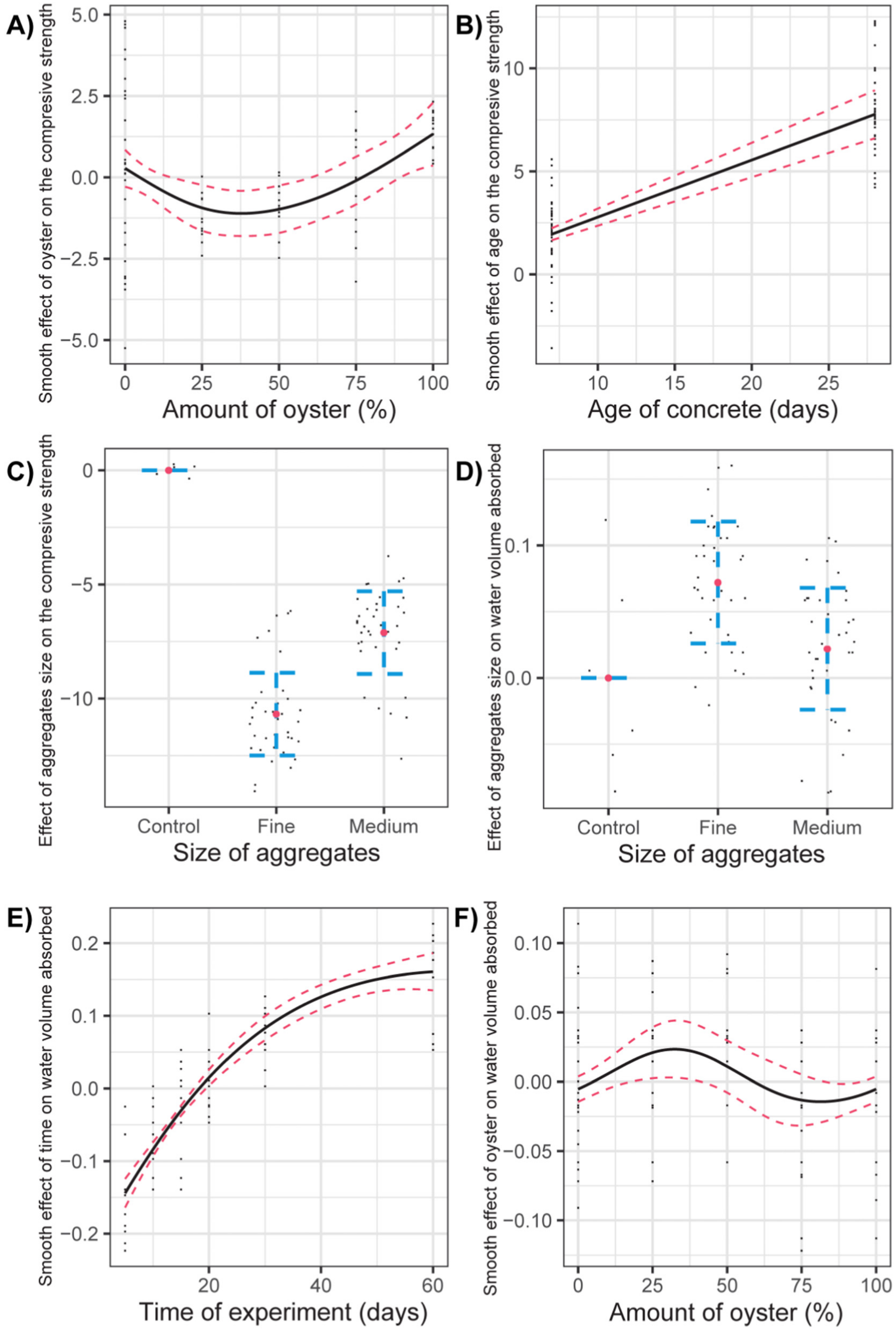

Fig. 6. Plots related to the effects of covariates on the compressive strength (panels A, B, and C) and volume of water absorbed (panels D, E, and F) corresponding to GAM models fitting. (A) Smooth effect of oyster percentage on the compressive strength. (B) Smooth effect of concrete age on the compressive strength. (C) Linear effect of aggregate size on the strength. (D) Linear effect of aggregates on water volume absorbed. (E) Smooth effect of experimental time on water volume absorbed. (F) Smooth effect of oyster percentage on water volume absorbed.

high oyster content (M1 and M2). Consequently, the following multivariate linear regression model has been fitted, ensuring all the variables are significantly different from zero (*p*-value of t statistic <0.05):

$$Volume = -0.2436 + 0.0884 \cdot Aggregates[Fine] + 0.0384 \cdot Aggregates[Medium] + 0.1293 \cdot \log(Time) - 3.4 \cdot 10^{-6} \cdot Oyster^2; R^2 = 81.8\% . \quad (4)$$

The effects of the covariates on the volume of water absorbed can be observed in Fig. 7e–g. When the time of exposition to water is raised, the volume seems to increase in a logarithmic way (Fig. 7e). Fig. 7f shows the role of aggregate size. When a fine aggregate is used, the absorbed volume of water tends to increase significantly by 0.084 ml. However, if a medium aggregate is used, a 0.0384 ml increase in water indicated by the formula cannot be considered significantly different from zero (p-value = 0.106084 > 0.05 and the intervals of Control and Medium in Fig. 7f are partially overlapped).

In other words, it is not possible to affirm that the volume of water absorbed when medium aggregate is added is different from that corresponding to the control sample. This supports the feasibility of replacing aggregates with oyster shells. Moreover, a x^2 type polynomial has been fitted to properly reproduce the polynomial (opened downwards) effect of oyster percent as can be observed in Fig. 7g. This model explains 81.8 % of the overall variability of the volume of water absorbed. Fig. 7h shows that the time of exposition to water is the covariate with the greatest influence, accounting for 91.9 % of the total variability explained. In contrast,

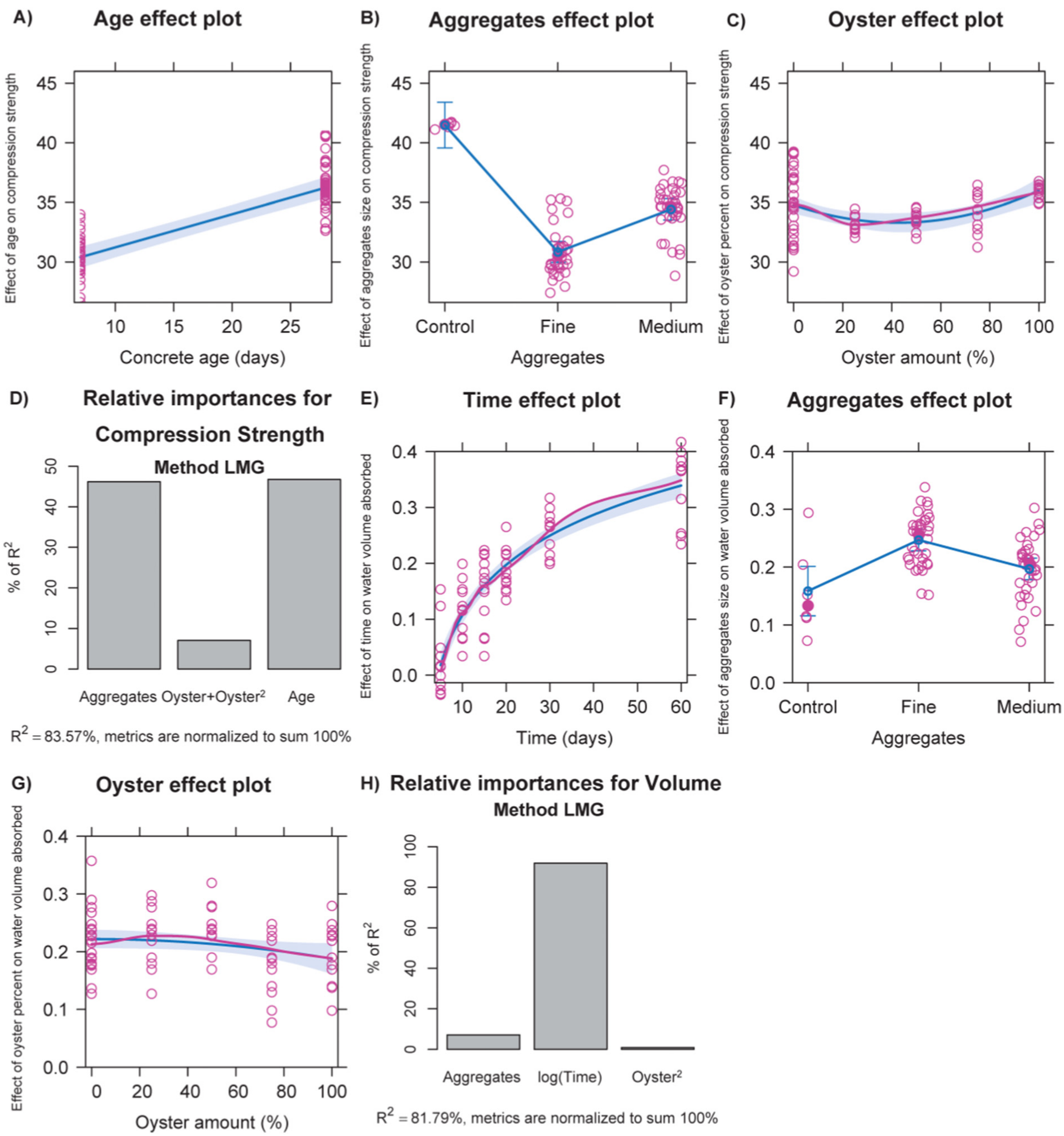

Fig. 7. Panels A–C show the effect plots for the multivariate linear regression model to explain the compressive strength depending on concrete age, aggregate size and oyster amount, respectively. Panels E–G show the effect plots of the multivariate linear regression model to explain the water absorbed depending on time, aggregate size and oyster percentage, respectively. Panels D and H account for the relative importance of these covariates, in terms of R^2, in explaining the compressive strength and volume of water absorbed, respectively. The lines in blue represent the model covariate effects with confidence bands, whereas the pink lines are those effects fitted by a nonparametric model (loess). The closer the pink and blue lines are, the closer the model is to the observations.

aggregates size explains 7.2 % and the oyster percentage (as a polynomial function), the remaining 0.9 %. Therefore, although it is not the most influential design parameter, the amount of calcite from oyster shells significantly influences the concrete's compressive strength. Compared to its effect on compressive strength, the effect of the oyster percentage on the volume of water absorbed is much smaller, although significant.

The two multivariate linear regression models can be used to estimate the compressive strength and water absorption from the design parameters values. Moreover, these models can make it easier to understand the role of each design parameter or covariate on these CTQ variables. Their estimates also point to design parameters that correspond with a medium aggregate size, a high calcite addition (>87.5 %) and a calcite that mostly comes from oyster shell (>75 %).

3.3. Multi-criteria analysis results

The results obtained with both the SAW and VIKOR methods are included in Table 13. However, Table 14 has been produced to make it easier to compare mixtures as well as discuss the results. It shows the position that each mixture occupies in a ranking that increases. Only the best sample for each mixture was considered. In the particular case of VIKOR, only the results for Q (Appendix A) were taken into account.

From Table 14, it is clear that both methods identified the same two best alternatives (M1 and M2), although they occupy different positions in each ranking. These results are in line with the ones obtained in the statistical analysis, supporting the use of mixtures with a predominance of calcite (oyster, scallop). This is the case even though two new indicators were considered in the multi-criteria analysis. Mixture M5 came to occupy the third position in both rankings. This alternative presents a considerable amount of clam shell (aragonite), Table 3. However, its position is due to acceptable results in the mechanical properties, together with remarkable performances in terms of difficulty of the crushing process- only surpassed by three alternatives, one of them with no substitution aggregates (M0)- and environmental waste (50 % of scallop).

Table 13
Results obtained with the SAW and VIKOR methods. Source: authors' own.

Mixture	SAW	VIKOR		
	V	*S*	*R*	*Q*
M0 (sample 1)	0.6025	0.3975	0.3889	0.6854
M0 (sample 2)	0.6087	0.3913	0.3889	0.6774
M0 (sample 3)	0.6064	0.3936	0.3889	0.6803
M1 (sample 1)	0.7154	0.2846	0.1026	0.0733
M1 (sample 2)	0.7249	0.2751	0.0963	0.0508
M1 (sample 3)	0.7380	0.2620	0.0808	0.0085
M2 (sample 1)	0.7110	0.2890	0.1259	0.1169
M2 (sample 2)	0.7417	0.2583	0.0855	0.0113
M2 (sample 3)	0.7445	0.2555	0.0948	0.0227
M3 (sample 1)	0.5638	0.4362	0.1667	0.3753
M3 (sample 2)	0.5506	0.4494	0.1667	0.3926
M3 (sample 3)	0.5518	0.4482	0.1667	0.3910
M4 (sample 1)	0.5103	0.4897	0.2222	0.5353
M4 (sample 2)	0.4955	0.5045	0.2222	0.5546
M4 (sample 3)	0.5076	0.4924	0.2222	0.5389
M5 (sample 1)	0.7290	0.2710	0.1111	0.0695
M5 (sample 2)	0.7201	0.2799	0.1111	0.0810
M5 (sample 3)	0.7339	0.2661	0.1111	0.0630
M6 (sample 1)	0.4097	0.5903	0.2222	0.6667
M6 (sample 2)	0.4077	0.5923	0.2222	0.6694
M6 (sample 3)	0.4163	0.5837	0.2222	0.6581
M7 (sample 1)	0.3862	0.6138	0.2222	0.6974
M7 (sample 2)	0.3616	0.6384	0.2222	0.7295
M7 (sample 3)	0.3700	0.6300	0.2222	0.7185
M8 (sample 1)	0.3958	0.6042	0.2222	0.6849
M8 (sample 2)	0.3886	0.6114	0.2222	0.6943
M8 (sample 3)	0.4002	0.5998	0.2222	0.6791
M9 (sample 1)	0.4126	0.5874	0.2222	0.6630
M9 (sample 2)	0.4147	0.5853	0.2222	0.6601
M9 (sample 3)	0.4082	0.5918	0.2222	0.6686
M10 (sample 1)	0.4340	0.5660	0.2222	0.6350
M10 (sample 2)	0.4254	0.5746	0.2222	0.6462
M10 (sample 3)	0.4407	0.5593	0.2222	0.6262
M11 (sample 1)	0.5271	0.4729	0.1570	0.4075
M11 (sample 2)	0.5303	0.4697	0.1570	0.4032
M11 (sample 3)	0.5016	0.4984	0.1678	0.4584
M12 (sample 1)	0.5043	0.4957	0.2222	0.5432
M12 (sample 2)	0.4986	0.5014	0.2222	0.5507
M12 (sample 3)	0.5003	0.4997	0.2222	0.5484

Table 14
Ranking of mixtures according to the SAW and VIKOR methods. Source: author's own.

Mixture	Position	
	SAW	VIKOR (*Q*)
M0	4	11
M1	2	1
M2	1	2
M3	5	4
M4	7	6
M5	3	3
M6	10	9
M7	13	13
M8	12	12
M9	11	10
M10	9	8
M11	6	5
M12	8	7

Mixture M7 occupied the last position according to both methods, conditioned by its intermediate results in almost all indicators, far from the best possible values. M0 is the mixture that does not include shells; it therefore obtained the worst possible results for the environmental indicator. Nevertheless, it had the best results for mechanical properties. These two opposing trends make M0 better positioned than M7 (or other mixtures with aggregate substitutions), but far from the best two alternatives. In fact, M0 is the sample that has undergone the greatest change in the position of both rankings. However, if new classifications were created through the VIKOR method based on S and R parameters (Table 13), M0 would occupy a similar position to the one obtained with SAW.

Finally, it is possible to say that both methods provided similar classifications. This suggests that the processes followed and the results obtained are both robust and consistent. On the other hand, the reader should bear in mind that slight changes in the weights here proposed would lead to small differences in the numerical results (Table 13) and in the rankings (Table 14). Nevertheless, these differences should not be significant. Moreover, major changes in weights would go against sustainability, the circular economy and the authors' experience in conducting the tests.

4. Conclusions

Among regions with relatively low pollution levels, Galicia (NW Spain) stands out for its bivalve mollusc production. Nevertheless, once these bivalves are harvested, a purification process is necessary to stem health risks through faecal contamination. This process generates waste during the transport and storage phases, due to individual mortality, as well as in the stages when pollutants are separated and eliminated.

The present work proposes to convert the residuals produced from shells containing calcic carbonate, $CaCO_3$, with a predominance of calcite and aragonite into by-products, to produce concrete for green artificial reefs (GAR). Currently, shells from oysters, clams, mussels and scallops are not extensively recycled, which can have visual impact on the landscape and mean that an opportunity for the circular economy is lost.

This study presented an analysis of the shells and proposed a range of mixtures to be employed as aggregates for concrete. This is the first time that the mortality percentages corresponding to each purification process phase have been estimated. This is also the first time that the use of waste from bivalve purification has been related to the process of determining the most suitable concrete mixtures. The granulometry, specific surface, specific gravity and composition of the shells were analysed. Mechanical tests were carried out to characterise the compressive strength and superficial absorption. A statistical analysis was developed to analyse the compressive strength and water absorption depending on the shell type, proportion and granulometry. Finally, a multi-criteria analysis was carried out to determine the most suitable alternative using indicators that were not considered in the statistical analysis. Although these statistical and multi-criteria techniques had been developed many years ago, this is the first study to have applied them in this way.

The statistical analysis suggests that the compressive strength of concrete depends on the age of the concrete, aggregate size, percentage of calcite and precedence of calcite (oyster or scallop). Particularly, the compressive strength seems to rise slightly when the oyster percentage is increased. Lower water absorptions are reached when a high proportion of calcite (>87.5 %) is presented, with oyster (≥75 %) also prevailing over scallop aggregates. The mixtures M1 and M2 present a suitable equilibrium between a relatively high compressive strength and a low water absorption (comparable with the control formulation). In accordance with these results, the design parameters should correspond to a medium aggregate size and high calcite (>87.5 %). Moreover, this calcite should proceed from oyster shell (>75 %).

The multi-criteria analysis considered the following aspects: compressive strength (7 days), compressive strength (28 days), water absorption by capillarity, difficulty of the crushing process and environmental relevance of the different types of waste. Two different procedures were employed to validate the obtained results. These methods are: the simple additive weighting (SAW) and VlseKriterijumska Optimizacija I Kompromisno Resenje (VIKOR) methods. Using these two procedures, a classification of the different mixtures was established. Both methods identified the same options as being the most suitable (M1 and M2). These results are in line with those from the statistical analysis, since both M1 and M2 are mixtures in which the medium aggregates are substituted with shells- mainly oyster- with a predominance of calcite. This was observed even with the addition of new indicators that had not been not taken into account in the statistical analysis. This factor highlights the validity of the obtained results.

CRediT authorship contribution statement

Luis Carral Couce ***Conceptualization***; ***Data curation***; ***Formal analysis***; ***Funding acquisition***; ***Investigation***; ***Methodology***; ***Project administration***; ***Supervision***; ***Validation***; ***Visualization***; ***Roles/Writing – original draft***;

M. Isabel Lamas-Galdo ***Data curation***; ***Formal analysis***; ***Investigation***; ***Writing – review*** & ***editing***

José Luis Mier Buenhombre ***Conceptualization***; ***Data curation***; ***Formal analysis***; ***Roles/Writing – original draft***

Juan José Cartelle Barros ***Conceptualization***; ***Data curation***; ***Formal analysis***; ***Visualization***; ***Roles/Writing – original draft***; ***Writing – review*** & ***editing***

Salvador Naya ***Conceptualization***; ***Data curation***; ***Formal analysis***;

Javier Tarrio-Saavedra ***Conceptualization***; ***Data curation***; ***Formal analysis***; ***Methodology***; ***Software***; ***Roles/Writing – original draft***; ***Writing – review*** & ***editing***

Data availability

Data will be made available on request.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.159095.

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