Green Aquaculture Intensification

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 773330

Innovative circular processes for bivalve shells valorisation

Martiña Ferreira, Diego Méndez & Leticia Regueiro
ANFACO-CECOPESCA

June 2021

Hello and welcome again to this unit coordinated by Anfaco, and produced by Martiña Ferreira, Diego Méndez and Leticia Regueiro.

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Part 3: Current examples of shellfish by-product valorisation

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In this third part we look at other current examples of shellfish by-product valorisation.

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Current uses: Livestock feed supplement

- Calcium supplementation is used to improve the health of livestock, particularly bone health
- Also in laying birds is used as a supplement to improve the quality and strength of egg shells
- Also some studies showed that it was an effective supplement for broiler chickens

References:

- Scott M.L., S.J. Hull, & P.H. Mullenhoff. 1971. The calcium requirement of laying hens and effects of dietary oyster shell upon egg shell quality. Poultry Sci., 50 (1971), pp. 1055-1063
- Miller, P. C. and Sunde, M. L. (1975). The effect of various particle sizes of oyster shell and limestone on performance of laying leghorn pullets. Poultry Science 54: 1422–1433
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- Pizzolante, C. C., Saldanha, E. S. P. B., Laganá, C., Kakimoto, S. K., & Togashi, C. K. (2009). Effects of calcium levels and limestone particle size on the egg quality of semi-heavy layers in their second production cycle. Revista Brasileira de Ciência Avícola, 11(2), 79-86.
- Saunders-Blades JL, MacIsaac JL, Korver DR, Anderson DM. The effect of calcium source and particle size on the production performance and bone quality of laying hens. Poult Sci. 2009 Feb;88(2):338-53. doi: 10.3382/ps.2008-00278.

As mentioned in Part 1, when we gave the example of Abonomar. Calcium supplementation is used to improve the health of livestock, particularly bone health, but also in laying birds as a supplement to improve the quality and strength of egg shells.

Calcium supplementation has been used widely for laying hens over several decades, where calcium carbonate sourced from mined limestone is commonly used. Several studies have tested the effect on poultry of oyster shell-derived calcium carbonate in comparison to a more standard limestone enriched diet. These found that as well as being a potentially cheaper source of calcium carbonate, crushed oyster shell at optimal dosage can perform equally to limestone as a form of calcium supplementation across a number of tested parameters.

A study from Scott and colleagues found that partially substituting oyster shells for limestone both increased the egg production rate and egg shell strength of laying hen eggs and other authors observed similar results with oyster shell supplementation, showing increased egg shell weight and thickness.

A later study by Miller and Sunde found no significant differences between oyster shells, clam shells, limestone, aragonite, or eggs shell supplementation across a number of hen and egg performance indices. In 1990, a study by Aletor and Onibi suggested that oyster shells were both a cheaper and more effective calcium supplement than limestone in cotton-seed cake feed mix for broiler chickens. Chickens fed on an oyster shell-enriched diet showed higher weight gain capacity than those fed on an unenriched diet. However, another later study found that calcium source had no appreciable effect on calcium utilization and chick performance when comparing bivalve shells, oyster shells, and limestone sources. Moreover, that study found particle size was a better predictor of weight gain, feed conversion, and tibial ossification than calcium source, with finer particulate calcium performing better.

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Current uses: Agricultural liming agent

- The second major market, including neutralisation of soils and metals bioremediation
- Liming is an important activity with several benefits such as reduce acidity and improve fertility.
- Liming action can be also a carbon sink mechanism
- The toxicity of the salt related to crushed shells was studied and no toxicity was demonstrated
- Use of crushed oysters improved soil status promoted microbial populations, increasing nutrient cycling

Chang Hoon Lee, Do Kyoung Lee, Muhammad Aslam Ali, Pil Joo Kim. 2008.
Effects of oyster shell on soil chemical and biological properties and cabbage productivity as a liming materials. Waste Management, Volume 28, Issue 12, Pages 2702-2708.
https://doi.org/10.1016/j.wasman.2007.12.005.

The second major market for shells is, again, in the agricultural sector, but involving the neutralisation of acidic and metal contaminated soils. Generally referred to as liming, the practice involves treating soil or water with lime in order to reduce acidity, and improve fertility and oxygen levels.

Liming dates back to the first and second centuries BCE, and has subsequently been prevalent in many societies. The practice of liming is well known as having numerous positive effects on the productivity of agricultural crop yields, and can also have longer-term positive effects on soil quality and structure. Further, although still unresolved, it has been suggested that under certain conditions, the application of a liming agent to agricultural land can act as a net carbon sink mechanism, being beneficial from the environmental point of view to avoid impact of the global warming potential.

Crushed mollusc shells from the aquaculture industry can be a viable replacement for more commonly used mined calcium carbonate, such as limestone. A number of studies have quantified various effects of the application of crushed mollusc shells to agricultural land. In Korea, for instance, crushed oyster shells were applied to two acidic soil types at a variety of rates, and assessments of Chinese cabbage yield, and soil pH and nutrient metrics, were analysed. This study found that the crushed oyster shell meal significantly increased soil pH, improved soil nutritional status metrics including available phosphate and organic matter mass. Previous concerns regarding elevated salt levels were tested, and despite a slight increase in soil Na concentrations, no signs of toxicity damage were observed in the cabbage. Further, improved soil status promoted microbial populations, increasing nutrient cycling.

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Current uses: De-icer grit

- Chlorine-based compounds, such as rock salt (NaCl), are commonly used as de-icing chemicals.

- Chlorine-based road grits could damage the urban environment due to their corrosive effects.

- Calcium magnesium acetate or any calcium acetate could be environmental-friendly potential alternatives as road grit

- The use of shells as calcium donor in the formation of calcium acetates could be also an alternative use for shells valorisation.

Hartl, W., & Erhart, E. (2002). Effects of potassium carbonate as an alternative road de-icer to sodium chloride on soil chemical properties. Annals of applied biology, 140(3), 271-277.

Chlorine-based compounds, such as rock salt, are commonly used as de-icing chemicals.
However, it is well known that chlorine-based road grits could damage the urban environment, and also the natural one, due to their corrosive effects. In fact, they are forbidden in airports, as they can damage aircraft.
In this sense, calcium magnesium acetate or any calcium acetate could be an environmentaly-friendly potential alternative as road grit. The use of shells as calcium donor in the formation of calcium acetates could therefore be an alternative method of shell valorisation. The use of potassium carbonate as a de-icer and the combination of scallop shells mixed with apple pomace waste from Aomori Prefecture in Northern Japan was reported by Hartl and Erhart in 2002.

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Current uses: Water treatment

- The main use of shells in water treatment is for heavy metal removal in wastewater treatment facilities, since the calcium carbonate rich powder is good as a lead (Pb) sorbent, whilst the use of mixed shells rich in both calcite and aragonite should be optimised for heavy metal removal. Another study indicated that the shell dust coming from invasive snail (*Physa acuta)* could act as an effective cadmium (Cd) sorbent.

- Besides heavy metals, calcareous shells have been previously tested as nitrate, sulphate and/or phosphate sorbents. For instance, the use of shells for carbon sequestration has been studied by several authors, highlighting that a previous pre-treatment via calcination or pyrolisation to convert the shells in calcium oxide (CaO) is required.

- Du, Y., Lian, F., & Zhu, L. (2011). Biosorption of divalent Pb, Cd and Zn on aragonite and calcite mollusc shells. Environmental Pollution, 159(7), 1763-1768.
- Hossain, A., & Aditya, G. (2013). Cadmium biosorption potential of shell dust of the fresh water invasive snail Physa acuta. Journal of Environmental Chemical Engineering, 1(3), 574-580.
- Ma, K. W., & Teng, H. (2010). CaO powders from oyster shells for efficient CO2 capture in multiple carbonation cycles. Journal of the American Ceramic Society, 93(1), 221-227.
- Castilho, S., Kiennemann, A., Pereira, M. F. C., & Dias, A. P. S. (2013). Sorbents for CO_2 capture from biogenesis calcium wastes. Chemical Engineering Journal, 226, 146-153.
- Monneron-Gyurits, M., Joussein, E., Soubrand, M., Fondanèche, P., Rossignol, S. (2018). Valorization of mussel and oyster shells toward metakaolin-based alkaline activated material. Applied Clay Science 162, 15–26

The main use in water treatment of shells is related to heavy metal removal in wastewater treatment facilities, since the calcium carbonate rich powder is good as a lead sorbent, whilst the use of mixed shells rich in both calcite and aragonite should be optimised for heavy metal removal.
The shell preparation should be optimized via simple technological treatments to avoid expensive end-products. For instance, the same authors suggested a process based on washing, airdrying and pulverisation.
Moreover, another study indicated that the shell dust coming from invasive Physa acuta could act as an effective cadmium sorbent.
Besides heavy metals, calcareous shells have been previously tested as nitrate, sulphate and/or phosphate sorbents. For instance, the use of shells for carbon sequestration has been studied by several authors, highlighting that a previous pre-treatment via calcination or pyrolisation to convert the shells in calcium oxide is necessary. This "ad hoc" product displays a good performance; however, pyrolisation of shells may require heating over 400 ºC, which makes this solution not sustainable at large scale in terms of costs and environmental impact. Some studies, have worked with uncalcined or unpyrolysed shells that could represent a low-cost solution.

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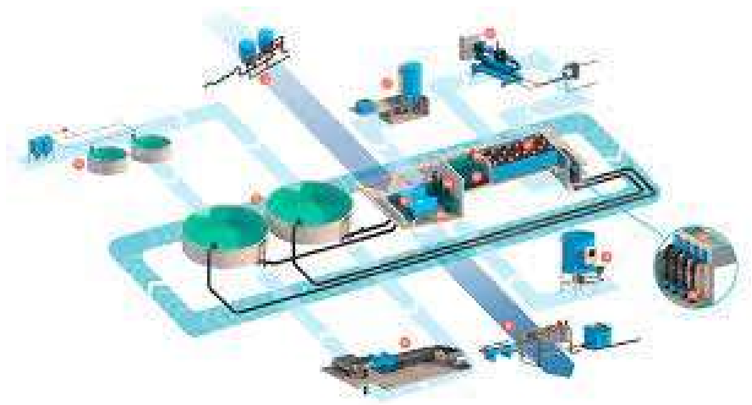

Current uses: Aquaculture water treatment

-Suitable material to remove nutrients from wastewaters discharged to natural environments

-Some studies showed the possibilities to be used in RAS systems

-Other studies showed the efficiency for phosphorous removal mainly using calcined shells

Yen, H. Y., & Chou, J. H. (2016). Water purification by oyster shell bio-medium in a recirculating aquaponic system. Ecological Engineering, 95, 229-236.
Buzin, F., Dupuy, B., Lefebvre, S., Barille, L., Haure, J. (2015). Storage of Pacific oysters Crassostrea gigas in recirculating tank: ammonia excretion and potential nitrification rates. Aquacultural Engineering 64, 8-14.

As previously mentioned, the physico-chemical properties of bivalve shells can also be exploited for the removal of dissolved nitrogen and phosphorus; important pollutants discharged by aquaculture facilities. Studies have demonstrated that oyster shells are a suitable material for the uptake of ammonia nitrogen and phosphorus from municipal wastewater, and are also appropriate to remove nutrients from wastewaters discharged to natural environments such as wetlands. Nevertheless, reports about the use of shells to treat water in aquaculture systems are scarce. Two studies described oyster shells used as biofilter medium in recirculation aquaculture, demonstrating an efficient water treatment and nitrification in an aquaponics setup combining oyster shells as biofilter followed by a cultivation of water spinach. Oyster shells support the growth of bacteria involved in nitrification. As for phosphorus uptake, the performance of adsorbent materials is apparently related to their chemical composition and structure. Iron-rich materials such as fly ash or bauxite are particularly efficient, but treatment with lime or other cheap carbonate sources is a low-cost method to remove phosphorus from wastewater, based on the precipitation of hydroxyapatite produced by the reaction of phosphate and dissolved calcium. Since bivalve shells are rich in calcium carbonate, they could also be potentially used to remove phosphorus from wastewater and particularly aquaculture effluents. Some authors performed experiments with calcined and non-calcined mussel shells to uptake dissolved phosphorus from water samples. Lab-scale experiments showed a higher uptake capacity in calcined samples, of around 600-800 mmol of phosphorous per kilogram. This is due to calcination of shells at 500 ºC or higher, which transforms the crystalline structure of calcium carbonate from aragonite to calcite; moreover, part of the calcium carbonate is transformed into the much more soluble calcium oxide, thus enhancing the reaction with phosphate and the precipitation of hydroxyapatite. In non-calcined shells, adsorption is the predominant mechanism of phosphorus removal, and therefore the process is mostly limited to the shell-water interface.

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Current uses: Green roofing

- Another potential use in the building industry is the incorporation of shells into green roofing structures
- They can help with the neutralisation of acid rain, and the reduction of heavy metal contamination in drainage water
- There are two forms of green roofs: extensive and intensive.
- Both types of roof are designed with the same principal layers: vegetation, growing medium, filter membrane, drainage layer, root barrier, waterproofing membrane.

Another potential use in the building industry is the incorporation of shells into green roofing structures, since they can help with the neutralisation of acid rain, and the reduction of heavy metal contamination in drainage water.
Green roofs, also known as living roofs, have seen a surge in popularity in the last decade, particularly in urban areas, as there is a growing conscience of the importance of green spaces for environmental health. Green roofs can have a number of beneficial effects: increasing habitat space for wildlife, mitigating urban heat island effects, providing building insulation, providing rainwater absorption and improved waste-water management, as well as potentially providing a stress-reducing and attention-increasing environment for those in proximity.
Green roofs typically come in two forms: extensive and intensive. The two are differentiated according to the depth of planting medium used, and the need for maintenance. Type 1: extensive roofs having 10-25% of the growing medium of type 2: intensive roofs. Extensive roofs are designed for minimal maintenance, whereas intensive roofs can be more versatile but require maintenance as a garden would. Both types of roof are designed with the same principal layers: vegetation, growing medium, filter membrane, drainage layer, root barrier, waterproofing membrane. A potential use of waste mollusc shells is as the drainage layer in green roofing structures. The drainage layer is important in carrying away excess water from the

roof. It is a 3D structure between the filter layer and the waterproof membrane. Whole shells maybe ideal for such a structure, as when heaped they provide a complex 3D structure to aid drainage

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Current uses: shells in the building sector

- Whole oyster shells are used for simple wall structures in coastal villages in China, and crushed scallop shells have been used as a simple path aggregate on the Island of Mull in Scotland.

- In France, a study investigated the incorporation of crushed *Crepidula* shells into pervious concrete mixes and concluded that shell incorporation did not have an adverse effect on the concrete's mechanical strength, and increased porosity allowed for better water permeability, an important characteristic of pervious concretes.

Shells have been used as a simple material for construction, or are incorporated into aggregate and mortar mixes due to their characteristics that might make them suitable for certain construction aggregates. For example, whole oyster shells are used for simple wall structures in coastal villages in China, and crushed scallop shells have been used as a simple path aggregate on the Island of Mull in Scotland.
In France, a study investigated the incorporation of crushed *Crepidula sp*. (slipper limpet) shells into pervious concrete mixes, and concluded that shell incorporation did not have an adverse effect on the concrete's mechanical strength, and increased porosity allowed for better water permeability, an important characteristic of pervious concretes. Further studies have found similar viability of shell incorporation in various aggregate mixes.

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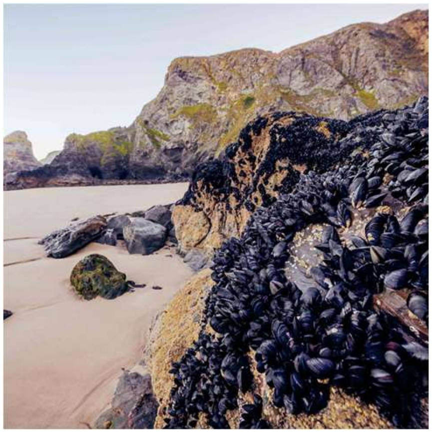
Current uses: shells in the building sector

- More recently, In Spain, Galician mussel shells have been tested for their suitability in aggregate mixes.

- The Biovalvo project (https://proyectobiovalvo.wordpress.com/) carried out by the University of Coruña has demonstrated that mussel shells thermally processed at 135°C for 30 minutes can be used as aggregates for mass concrete. Percentages of substitution of up to 25% of natural aggregates by mussel shell aggregate (sand or gravel) are suitable for structural concrete.

- A study assessing the incorporation of mussel shell waste in Spain into mortars found that differences in particle microstructure between quarried limestone and mussel waste $CaCO_3$ resulted in mussel waste-derived mortars showing improved setting times and final strength.



Ballester, P., Mármol, I., Morales, J., Sánchez, L. (2007). Use of limestone obtained from waste of the mussel cannery industry for the production of mortars. Cement and Concrete Research 37, 559–564.

More recently, in Spain, in the Galician region, mussel shells have been tested for their suitability in aggregate mixes.
The Biovalvo project is an idea to provide mussel shells with a more "constructive" use
This project, coordinated at the University of La Coruña (Universidade da Coruña, UDC), is trying to exploit the insulating properties of this material in order to incorporate it into an innovative green building model.
The Biovalvo project has demonstrated that mussel shells, thermally processed at 135°C for 30 minutes, can be used as aggregates for mass concrete. Percentages of substitution of up to 25% of natural aggregates by mussel shell aggregate (sand or gravel) are suitable for structural concrete.
The potential use of shells in the cement industry has also been investigated. A study assessing the incorporation of mussel shell waste in Spain into mortars found that differences in particle microstructure between quarried limestone with rounded particles, and mussel waste calcium carbonate with elongated prismatic particles, resulted in mussel waste-derived mortars showing improved setting times and final strength.

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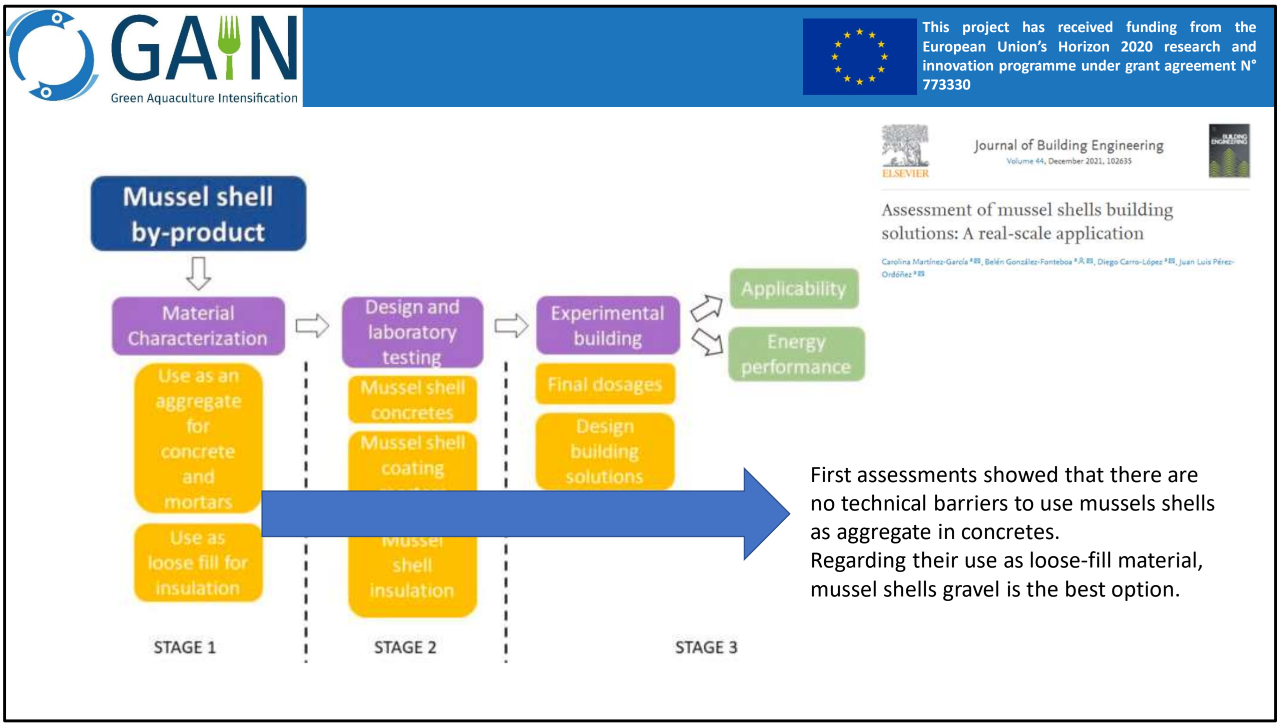
The Biovalvo project constructed a house, located in Mariñeiros, featuring walls, floor and roof using up to 75% shell material in their composition

Since its construction, the short-term output of the project regarding resistance capacity and wall insulation seems to have been very satisfactory. Researchers are currently focused on monitoring long-term behaviour and the aging process of these mortars. To do this they are subjecting the material to extreme environmental temperatures, high and low, and significant humidity levels, in order to calculate the amount of shells needed for the structure to become completely resistant and durable.

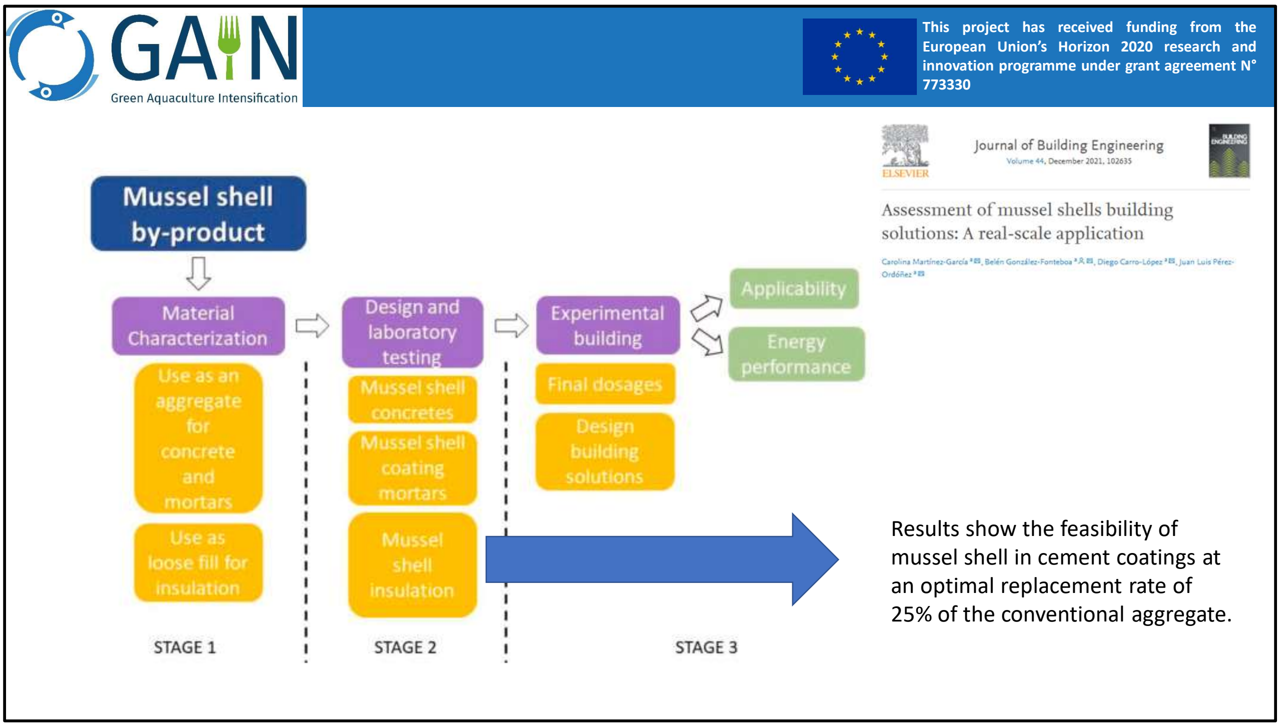
Continuing with the Biovalvo project, the main hotspot of the project is a building constructed with this mussel material. This is the cornerstone of their research and the symbol of this increasingly promising initiative. The house, located in Mariñeiros, features walls, floor and roof using up to 75% shell material in their composition instead of quarry sand, while other materials low in CO_2 emissions, such as clay or lime, replace cement to bind the mixture.

Since its construction, the short-term output of the project regarding resistance capacity and wall insulation seems to have been very satisfactory. Researchers are currently focused on monitoring long-term behaviour and the aging process of these mortars. How do they do it? By subjecting the material to extreme environmental temperatures, high and low, and significant humidity levels, in order to try and calculate through a series of sensors the amount of shells needed for the structure to become completely resistant and durable.



There are no technical barriers to use mussel shells as aggregate in concretes and coating mortars. Moreover, drying cracks are not observed in mussel shell concretes or in coating mortars. The appearance of the exposed mussel shell particles is very aesthetic and represents an opportunity to apply this type of aggregate.

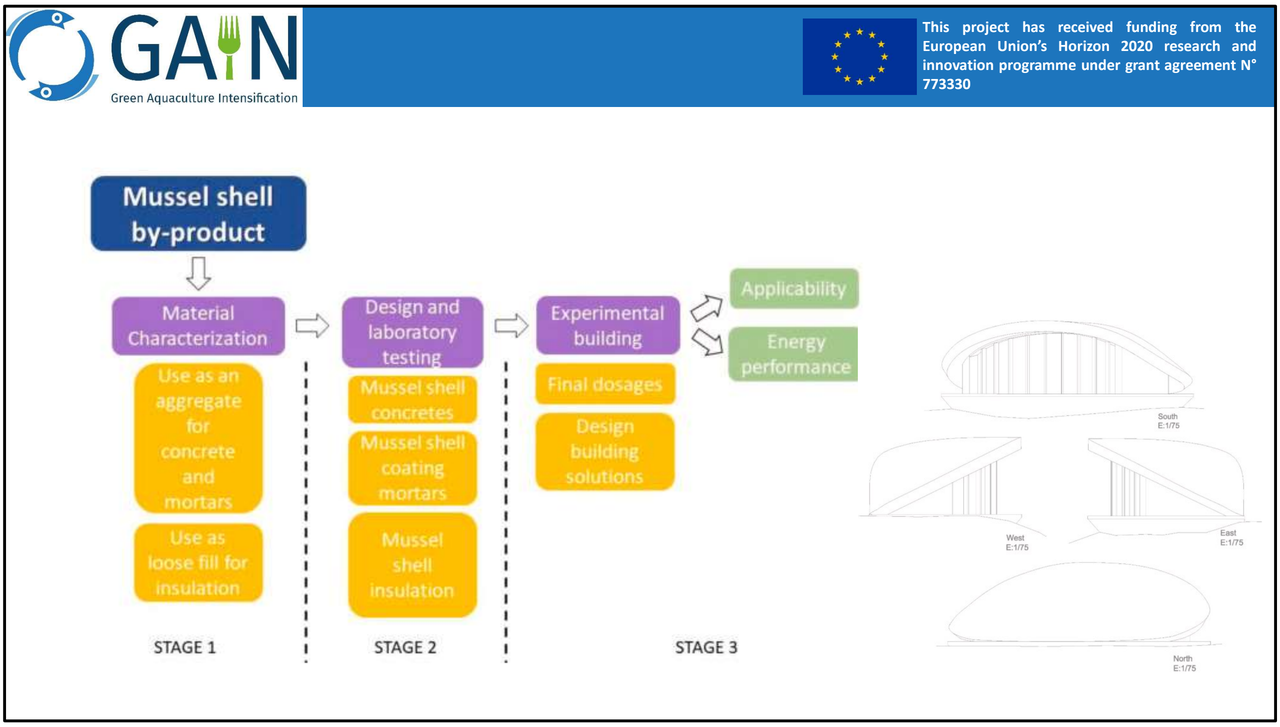
As loose-fill material, the mussel shell gravel is the best option for ground floor insulation, as its thermal conductivity value is appropriate. In addition, the waterproofing of the building in contact with the ground is solved. On the other hand, the compaction of mussel shells is something of a challenge in curved or thin spaces, so they should be combined with another type of insulation material in flexible form (batts or roll). In flat and straight cavities (walls, roofs and slabs), however, it could be a good solution with good thermal and acoustic performance.



Once the material was characterized and the results were promising, the next step was to design and validate the material in laboratory testing analysis.
The mussel shell was heat-treated at 135 °C for 30 minutes and then crushed and sieved to produce gravel and sand. The aggregate is composed mainly of calcium carbonate (>95%) with traces of organic compounds and small amounts of sulphate and chloride.
The first application that authors considered was the production of plain concrete. The results established that mussel shell replacement should be limited to 25% of fine or coarse aggregates, or 12.5% of both fine and coarse aggregates. With these percentages the concrete displays appropriate properties and an interesting aesthetic finishing with fragments of seashells.

The second application was mortars for coatings, in these case, authors considered that the 25%, 50% and 75% of the aggregate was replaced by shell aggregates. The binders considered were cement and lime that were studied as sustainable alternatives. The cement-based mortars agreed with the results in concrete with a recommended replacement rate of 25% as maximum. This limit is also the recommendation for the lime mortars, although with larger quantities the changes are not severe, and the finishing could be appealing. Mussel shell aggregates affect workability, density, and mechanical properties of coating mortars with both binders applied. Also, the capillary uptake was reduced along with the enhancement of water retention. This was attributed mainly to the organic matter content of mussel shells and also due to their flake shape. These two parameters also affect the carbonation of lime mortars; at young ages it was decreased while the total carbonated area was increased at old ages when compared with baseline.

Finally, the third application considered was to use mussel shell aggregate as loose fill material. This mussel shell material has been found suitable for using as building insulation material. Mussel shell confined inside an enclosed space (e.g. a wooden box) has a thermal conductivity similar to that of a light conifer wood, so it can be considered a material with low thermal conductivity. In addition, the material displays an acoustic behaviour comparable to others commercialised insulation materials. The use for building solutions was studied in the third stage of this project.



The last step of this project was the erection of an experimental building that includes all the building materials described in this research: roof, walls, floor and foundation included mussel shells with very good outcomes. The results of this experience will be published in scientific papers although preliminary data are already known.

Regarding the energy performance, compacted mussel shells can be used as thermal insulation in a building with low energy consumption. When the geometry of the building allows for suitable air tightness, mussel shell insulation could be used in a designed passive house building.

Regarding installation, the mussel shell wall has a simple construction process: heavy machinery or specialized workers are not required, and the wood structures can be assembled in workshops. All these parameters define an unsophisticated solution to be used in auto-construction; however, it could be sold as a pre-assembled building kit for an easy installation.

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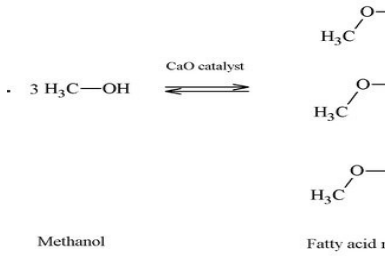
Calcium oxide catalysts

- Calcium oxide (CaO) is a widely used catalyst and chemical compound in a myriad of industrial applications. CaO can be formed via the calcination of $CaCO_3$

- Waste shells from aquaculture have been advocate as a low cost $CaCO_3$ source for the production of CaO for a variety of applications, particularly biodiesel production in developing countries.

- Oyster shells have been shown to be an effective heterogeneous catalyst in the conversion of soybean oil into biodiesel, whereas calcined waste cockle shells were good to catalyse the production of biodiesel from palm olein.
- Freshwater mussel shell was found to be a feasible catalyst in the conversion of Chinese tallow oil to biodiesel, and was able to catalyse 7 reaction cycles (Hu et al., 2011).

- Finally, oyster shell-derived calcium oxide was used to modify copper-based catalysts, and compared to commercial calcium oxide sources as a hydrogenation catalyst.



There are several innovative niche applications for shell waste described in the academic literature. These applications include those that require high-energy processing of Calcium carbonate, or those that require only small amounts of shells. Such applications are not likely to impact shell waste production from the aquaculture industry, but represent innovative circular economy developments, and could provide economic benefits in the future.
This is the case of the use of mussel shells as calcium oxide catalysts.
Calcium oxide is a widely used catalyst and chemical compound in a myriad of industrial applications. It can be formed via the calcination of calcium carbonate, a process that requires heating the material to in excess of 800 °C (sometimes in an oxygen enriched environment). Calcination results in the conversion of solid calcium carbonate to solid calcium oxide, liberating gaseous carbon dioxide in the process. Waste shells from aquaculture have been advocated as a low cost calcium carbonate source for the production of calcium oxide for a variety of applications, particularly biodiesel production in developing countries. Fatty acid methyl esters, called FAMEs, are a component of the biodiesel production, made by reacting oils and fats with an alcohol: a process called transesterification. The transesterification of oils and fats with methanol can be facilitated by a heterogeneous catalyst (as Calcium oxide), which provides a simplified and cheap albeit slow-reaction alternative to a

homogeneous catalyst (as for instance using Potassium hydroxide). Calcined oyster shells have been shown to be an effective heterogeneous catalyst in the conversion of soybean oil into biodiesel. Some studies calcined waste cockle shells (*Anadara granosa*) to catalyse the production of biodiesel from palm olein. Similarly, freshwater mussel shells were calcined, at 900 °C, then impregnated with deionized water and activated by heating to 600 °C, the resultant 'honeycomb-like' catalyst structure was found to be a feasible catalyst in the conversion of Chinese tallow oil to biodiesel, and was able to catalyse seven reaction cycles.
Finally, oyster shell-derived calcium oxide was used to modify copper-based catalysts, and compared to commercial calcium oxide sources as a hydrogenation catalyst. Results showed that oyster shell-derived calcium oxide was a more efficient methanol synthesis catalyst, with suggestions that shell-based impurities resulted in calcium oxide crystal defects that increased reaction surface areas, and thus reaction efficiency

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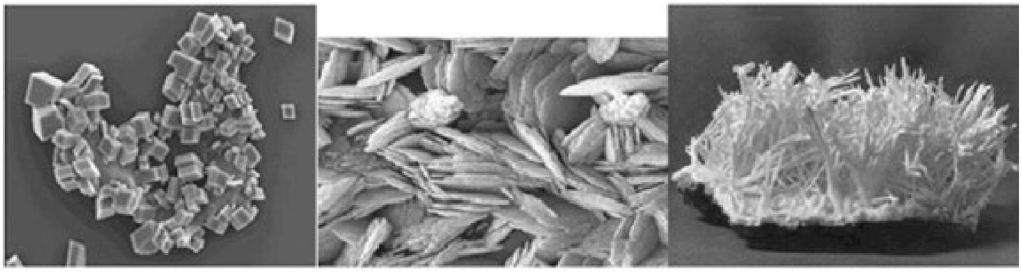
Biomedical and cosmeceutical

- Modern science has found that shells, particularly their organic protein matrix, can exhibit many properties that are of interest to the modern cosmetics and biomedical industry.
- The most widely discussed biomedical use for shells is in bone and tissue re-engineering
- The $CaCO_3$ powder acts as a substrate on which new osteoblasts can grow and secrete bone. For instance, nacre powder, from oyster *Pinctada maxima*, acted as a scaffold in bone reconstruction in human jaw defects, demonstrating their potential in bone engineering and augmentation applications.



Recent studies have found that shells, particularly their organic protein matrix, can exhibit many properties that are of interest to the modern cosmetics and biomedical industry. The following data summarises the academic literature advocating shell-use in biomedical and cosmeceutical applications.

The most widely discussed biomedical use for shells is in bone and tissue re-engineering. Powdered shell has been shown to have osteogenic properties, likely because of its biogenic origins. When placed into a human bone fracture, the calcium carbonate powder acts as a substrate on which new osteoblasts can grow and secrete bone. In 1997, groundbreaking maxillofacial surgery was performed on eight human patients with maxillary defects. Nacre powder, from the oyster *Pinctada maxima*, was found to promote bone formation, and act as a scaffold in bone reconstruction in human jaw defects.

More recent studies from 2016 and 2017, supported the potential for shell-use (particularly nacre), in bone engineering and augmentation. Further, researchers have suggested that shell could be converted to hydroxyapatite which is the major constituent of human bones.

On the image you can see the different type of crystals of various calcium carbonates, from the left to the right side, they are calcite, vaterite and aragonite.

Normally in the tissues are prepared with calcium carbonate -phosphate samples doped by microelements using the abovementioned polymorphous phases: calcite (rhombohedra structure), vaterite (hexagonal), and aragonite (orthorhombic). The last two phases are known to be metastable.

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Functional materials

- The previous slides have highlighted the potential for $CaCO_3$ shells to be converted to other compounds such as calcium oxide, calcium phosphate, or hydroxyapatite, for instance. These conversions open up further potential applications, and widen the potential uses of shells in industry.

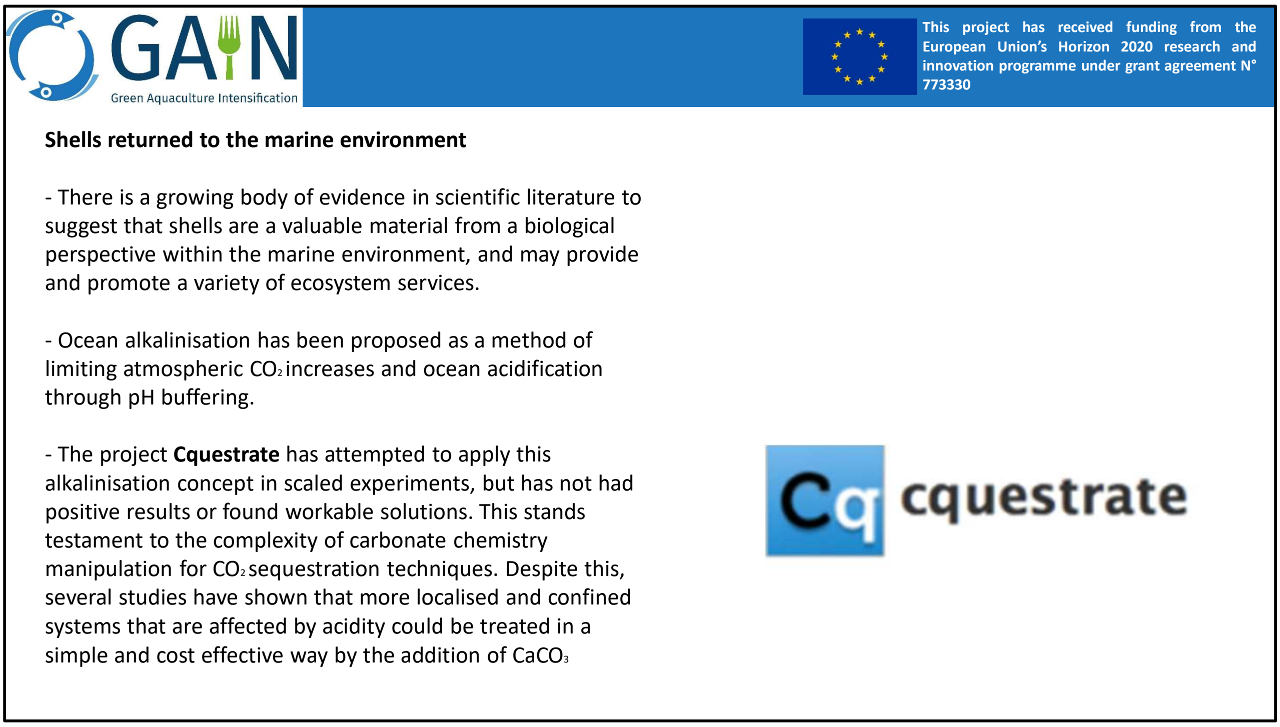
- Nacre, in particular, has inspired the field of nanocomposite materials for several decades due to its calcium carbonate organic matrix layered arrangements.

- There are a number of articles highlighting the potential use of waste shells from aquaculture in polypropylene and polymer composites. Waste blue mussel (*Mytilus edulis*) shells were used as a base material for $CaCO_3$ filler in polypropylene manufacture.

Looking at studies regarding biomedical or cosmeceutical applications, it is possible to conclude that the shells' potential to be converted to compounds such as calcium phosphate or hydroxyapatite could open up other applications in the near future, and widen the potential use of shells to several industries, applying the shells as functional materials.

Nacre, in particular, has inspired the field of nanocomposite materials for several decades due to its calcium carbonate - organic matrix layered arrangements. Whilst the field of synthetic biomimetics attempts to replicate the toughness of strength of shells via *de novo* assembly there is also interest in incorporating shell waste into various functional material recipes.

In addition, there are a number of articles highlighting the potential use of waste shells from aquaculture in polypropylene and polymer composites. Waste blue mussel (*Mytilus edulis*) shells were used as a base material for a calcium carbonate filler in polypropylene manufacture.



The preceding examples have shown that shells are already being utilised for various purposes, and highlight that there are further sustainable and niche applications for shells that have yet to be exploited. There is however, a growing body of evidence in scientific literature to suggest that shells are a valuable material from a biological perspective within the marine environment, and may provide and promote a variety of ecosystem services. Further, there are an increasing number of organisations, charities, and research groups that are already returning shells to the marine environment for conservation reasons.

Here are some examples, highlighting the potential ecosystem services that waste shells from aquaculture could provide by being returned to the marine environment by various methods. They raise and address the question of whether we should be solely seeking economic value from shells or whether shells also have inherent and enduring value when returned to the marine environment.

Ocean alkalinisation has been proposed as a method of limiting atmospheric carbon dioxide increases and ocean acidification through pH buffering. In the published literature, limestone is regularly cited as a potential liming agent. The efficacy of ocean alkalinisation techniques is debated, however, due to the volume/mass of buffering agent required.

Calcium carbonate buffers such as limestone are unlikely to be practical at large scale in the near future, with minerals such as Olivine holding greater potential. Several projects (for example the Project Cquestrate), have attempted to apply this alkalinisation concept in scaled experiments, but results were not very positive. This stands testament to the complexity of carbonate chemistry manipulation for carbon dioxide sequestration. Despite this, several studies have shown that more localised and confined systems that are affected by acidity could be treated in a simple and cost effective way by the addition of calcium carbonate.

GAIN
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End of Part 3
Thank you for you attention

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This is the end of part 3. We hope you have found it interesting. When you are ready, you can proceed to Part 4.