Investigation of Mechanical and Thermal Performance of Concrete with Scallop Shells as Partial Cement Replacement: Alternative Binder and Life Cycle Assessment

Yassine El Mendili * and Mohammed-Hichem Benzaama

COMUE Normandie Université—Laboratoire ESITC, 1 Rue Pierre et Marie Curie, 14610 Epron, France
* Correspondence: yassine.el-mendili@esitc-caen.fr; Tel.: +33-231-452-628

Abstract: The adverse environmental impacts of building materials can be achieved by reducing the amount of cement in cementitious composites, specifically when incorporating wastes as partial replacement for Portland cement. In this work, we substitute cement with shell by-products while keeping useful specific properties. Scallop shells are good candidates to replace part of the Portland cement as they contain calcium and are available in abundance. We present an experimental and numerical study on the mechanics, hygrothermal behavior, and life cycle analysis of scallop shell concrete. In the fresh state, the replacement of cement by up to 10 wt.% of scallop shells does not significantly affect mortar properties. The results indicate that including 10% shells represents a decrease of up to 40% in the environmental impact, depending on the category of impact considered. Furthermore, the addition of Scallop shells makes the material more porous, leading to the facilitation of moisture transfer.

Keywords: alternative binder; Scallop shells; microstructural characterization; mechanical and hygrothermal properties; waste valorization; life cycle assessment

1. Introduction

The reduction of fossil-based energy use continues to be the primary concern in all areas of research in the construction field. In 2017, energy usage in the construction sector accounted for 21% [1] of global total final consumption, ranking third behind the industry and transportation sectors; additionally, 9% [1] of global total final consumption energy was dissipated and never used. All these energy increases raise power production and, as a result, CO₂ emissions.

One of the most recent trends to counter the existing problems of increasing energy use and greenhouse gas emissions is to use low carbon materials, either by enhancing the insulation efficiency of the building structure envelope, and thereby reducing energy consumption, or by developing new low carbon materials.

Low-carbon construction materials are typically bio-based or created by minimizing the quantities of high carbon inputs, with the use of different types of wastes. One of the most available waste products in Normandy (France) is seashells. Indeed, they represent the largest volumes available, and the deposit is of the order of 200,000 tons [2]. The huge quantities of shellfish abandoned on the seashore and in the municipal garbage cans show that their use is not very frequent.

Concretes with partial replacement of cement by seashells can present a good solution to decreasing CO₂ emissions as well as providing adequate mechanical and thermal properties compared to usual concrete [2]. Seashells are composed of at least 95 % of calcium carbonates (CaCO₃), which is comparable to calcium carbonate contents in limestone powders used for Portland cement production [3]. As stated in the literature, the principal component of scallop shells (SS) is calcite (CaCO₃), which can be used as an additional cementitious material. The European standard EN 197-1 states that calcium...
carbonate (CaCO$_3$) or limestone can be incorporated up to 35% in Portland cement. CaCO$_3$ acts principally as an inert filler when the replacement level is above 5%, due to its low solubility [2].

Studies dealing with the feasibility of using seashells in concrete fabrication have increased in the last decade. The majority of works on shell concrete have been dedicated only to its mechanical behavior, such as Bouasria et al. [2,4], Varhen et al. [5], Neamitha et al. [6].

M. Bouasria et al. [2] used the Crepidula Fornicata shells (CR) and ferronickel slag (FNS) as a structural component and a partial replacement in mortar. Mortar mixtures using different percentages of FNS and CR shells were formulated and tested up to failure. The results showed that the partial replacement of cement by up to 30% of FNS-CR mix has no significant effect on the workability of the cement in the fresh state. However, with incorporation above 30%, a slight loss of workability was observed. Water absorption by these additives exhibiting high specific surface area is responsible for this loss of workability. The hygrothermal behavior and life cycle analysis (LCA) was not developed in this study.

The absorption and permeability of seashell concrete is rarely reported in previous studies and needs to be further investigated. There are three promising experimental studies in which the authors investigate the potential of cockle shell ash as a material for partial cement replacement [7–9]. Nor Hazurina et al. [7] present the absorption and porosity results of concrete produced with various cockle shell ash replacements in comparison with a standard concrete. It is clearly demonstrated that cockle shell ash reduces the absorption of concrete at low percentages of replacement (below 15%). However, the absorption is increased with increased seashell content (25% and 50%). The absorption and porosity results can be related to the amorphous calcium carbonate nature present in seashell ash [8]. At lower percentages of replacements, the ash particles interlock with each other and fill the gaps in the concrete matrix, which leads to a decrease in the porosity and absorption. However, at higher replacement level, voids are formed due to the aragonite shape of seashell ashes, resulting in higher porosity and absorption [8]. Furthermore, Othman et al. [9] showed that the permeability of the concrete mixtures with cockle shell ash was higher than in the control concrete after 28 days and 90 days of curing. However, at the age of 120 days, the water permeability of the concrete mix with cockle shell ash was lower, except for the 50% replacement ratio. Previous studies have evaluated either the physical and mechanical properties of shell concrete, but none have considered life cycle assessment and hygrothermal behavior both at the same time and at the building scale.

To our knowledge, apart from the few studies presented above, the hygrothermal behavior and life cycle analysis are not well reported on in the literature. S. Cao et al. [10] and S.S. Sui Jiang et al. [11] show the capacity of the Wufi Plus software for the study of the hygrothermal behavior at the building scale. WUFI Plus is an advanced commercial software that helps the user simulate the impact of the energy performance of a building by considering the effects of moisture and heat at the same time [11].

Motivated by these recent results, in this paper we present a hygrothermal and environmental analysis of concrete based on the partial substitution of cement by scallop shells. The life cycle analysis (Using SimaPro and Pleiades tools) and hygrothermal behavior at the building scale (Using Wufi Plus tools) are evaluated. The research questions corresponding to the objectives are:

- What it is the environmental effect of shell concrete?
- What is the environmental benefit from the substitution of cement?
- What is the hygrothermal performance of shell concrete at building scale?

The paper is organized as follows: the experimental device and the numerical model are presented in Section 2. Section 3 is dedicated to the analysis of the results and their discussion, followed by the perspectives and conclusions.
2. Materials and Methods

2.1. Methodology

In line with what has been already proposed in the literature, we have developed a new conceptual framework that summarizes and visualizes our research methodology. The conceptual study plan of our work consists of three main parts, as illustrated in Figure 1. Each part is composed of several steps. These will be explained in detail in the following sections.

![Conceptual study plan diagram](image)

Figure 1. Conceptual study plan.

2.2. Concrete Properties

Mechanical properties are determined on mortars and thermal properties on concretes. The scallop shell concretes used in this study for thermal measurements are composed of:
- CEM I 52.5 N cement with a density of 3.2 g·cm\(^{-3}\) and a fineness of Blaine of 4100 cm\(^{2}\)·g\(^{-1}\). Its d\(_{10}\), d\(_{50}\), and d\(_{90}\) were determined using a laser diffraction particle size analyzer and are 2.43, 14.22, and 38.48 µm, respectively (Figure 2b).
- Standardized sand according to EN 196-1-1.
- Crushed gravel 3/8 mm with a density of 2.65 g·cm\(^{-3}\) and an absorption coefficient of 0.66%.
- Scallop shells (SS) collected in Ouistreham (Normandy, France), cleaned, crushed, and ground. Before being crushed with a drum compactor, the seashells were washed and dried at 40 °C to remove any apparent meat traces and contaminants. The collected seashells aggregates were re-crushed by the Los Angeles abrasion machine and sieved through a 63 µm sieve in order to generate scallop seashell powder. The density and Blaine fineness were 2.68 g·cm\(^{-3}\) and 7890 cm\(^{2}\)·g\(^{-1}\) respectively. Its d\(_{10}\) and d\(_{90}\) were determined using a laser diffraction particle size analyzer and are 2.88, 22.78, and 49.48 µm, respectively (Figure 2a). The d\(_{50}\) for the CEM I 52.5 N was 14.22 µm and the SS was 22.78 µm. Cements have finer particle sizes than seashells. Finer size will
offer more specific surface area for an accelerated hydration reaction. The acceleration of the hydration process will result in a rapid development of concrete strength.

![Diagram](image1.png)

**Figure 2.** Particle size distribution of (a): Scallop shells and (b): cement used in this study.

Table 1. Calcium is the major element. The analysis also shows the presence of traces of S, Na, Mg, S, and Al (<0.4 wt.%).

| Element | O * | C * | Ca | Na | S | Mg | Si | Al | Cl | Total |
|---------|-----|-----|----|----|---|----|----|----|----|-------|
| (wt.%)  |     |     |    |    |   |    |    |    |    | 100   |
|         | 34.5 ± 2.8 | 12.6 ± 0.5 | 51.3 ± 1.6 | 0.4 ± 0.1 | 0.4 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.2 ± 0.1 | d.l.  |       |

Table 1. Chemical composition of SS obtained by energy dispersive spectroscopy on ground SS powders. * O and C are taken with caution as being low precision; d.l.: detection limit.

The elaborated concrete specimens are prismatic samples of 30 cm × 30 cm × 7 cm. All specimens were compacted on a vibrating table. The concretes were demolded after 24 h and then placed at 20 °C and 95% relative humidity for 28 days of curing (Figure 3).

![Images](image2.png)

**Figure 3.** Scallop shell concretes prepared for this study.

The mortars were made from CEM I 52.5 N cement and standardized sand. The 4 cm × 4 cm × 16 cm mortars were made with a water/cement ratio set at 0.5 and a
sand/cement ratio set at 3, according to EN 196-1. The samples were placed in a controlled atmosphere (20 ± 1 °C and 90% RH). Cement was replaced by 5 and 10% shell waste (SS).

The composition of the mortar and concrete mixtures is given in Table 2.

Table 2. Composition of the different mortar and concrete mixes (Kg m$^{-3}$).

| Mortar  | CM | SS5 | SS10 |
|---------|----|-----|------|
| Cement  | 450| 428 | 409  |
| Fine sand 0/3 | 1350| 1350| 1350 |
| Scallop shells | 0  | 22  | 41   |
| Water   | 225| 225 | 225  |

| Concrete | CC | SS5 | SS10 |
|----------|----|-----|------|
| Cement   | 350| 332.5| 315  |
| Fine sand 0/3 | 756| 756 | 756  |
| Gravel 3/8 | 980| 980 | 980  |
| Scallop shells | 0  | 17.5| 35   |
| Water    | 175| 175 | 175  |

2.3. Characterization Techniques

X-ray diffraction of the scallop powder was performed at room temperature on a D8 Advance Vario 1 Bruker (two-circle diffractometer, 0–2θ Bragg-Brentano mode, Cu Kα radiation: λ = 1.54059 Å). The identification was performed using the Crystallography Open Database [12] and quantification was achieved using MAUD software [13].

All Raman spectra presented in this study were recorded at room temperature using a Thermo DXR Raman microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA), with a 532 nm laser as an excitation source used for Vibrational analyses. Raman spectra were recorded at 1 mW and with an integration time of 30 s.

The thermal conductivity was analyzed using a system of Heat Flow meter NETZSCH (Model HFM 436 Lambda). The test sample, with prismatic dimensions of 30 cm × 30 cm × 7 cm, is placed between the cooling plate and the heater plate; the heat flows from the heater plate through the sample to the cooling plate from where it is carried off. The cooling and heater plate temperature is adjusted by a Peltier cryostat to establish a temperature gradient from the heater plate across the specimen of 10 ÷ 30 °C.

Specific heat capacity (C$\text{p}$) characterizes the ability of a material to store thermal energy. C$\text{p}$ measurements are performed with a Differential Scanning Calorimetry technique (DSC, NETZSCH STA 449 F3) according to the standard ISO 11357-4. Data are collected from −20 °C to 30 °C continuously with heating rate of 1 °C min$^{-1}$.

2.4. Test Methods

The specific surface area of each cement mixture used in this study was determined with the Blaine air permeability apparatus according to the ASTM C-204 test method [14]. Workability tests were carried out using a mortar maniabilimeter according to the NF P18-452 standard [15]. The initial and final setting time for all mixtures was measured according to the NF P 15–431 standard [16]. The compressive and three-point bending tests were conducted according to the EN 196-1 standard [17].

2.5. Model of Heat and Moisture Transfer in Building Envelopes

WUFI-PLUS is used to simulate the thermal and moisture behavior of the building and the moisture flow into the room through the envelope structure. It is the most complete heat and moisture simulation tool in the WUFI® software family [18]. In addition to simulating hygrothermal conditions in building components, WUFI® Plus simulates the indoor environment and is therefore suitable for addressing comfort and energy consumption in
buildings [18]. Simulation of the interaction between building usage and system technology allows for integral assessment of indoor climate, hygienic conditions, thermal comfort, indoor air quality, and damage to components as a function of heating and cooling loads, and the necessary effort to humidify/dehumidify [18]. The indoor air heat and moisture balance equations in Wufi Plus are as follows:

- **Heat balance Equation:**
  \[
  \rho C_p V \frac{\partial T(t)}{\partial \tau} = Q_{\text{in}(t)} + Q_{\text{ev}(t)} + Q_{\text{ds}(t)} + Q_{\text{f}(t)} + Q_{\text{HVAC}(t)}
  \]
  (1)

  where: \( Q_{\text{in}(t)} \) amount of heat dissipation from the indoor heat source (W), \( Q_{\text{ev}(t)} \) convective heat transfer between the inner surface of the envelope and the indoor air (W), \( Q_{\text{ds}(t)} \) heat that enters the room (W), \( Q_{\text{f}(t)} \) heat generated by the solar radiation entering the room through the door and window (W), \( Q_{\text{HVAC}(t)} \) heat supply or cooling capacity of the air conditioner (W).

- **Moisture equilibrium Equation:**
  \[
  \rho C_p V \frac{\partial W(t)}{\partial \tau} = W_{\text{in}(t)} + W_{\text{ev}(t)} + W_{\text{f}(t)} + W_{\text{HVAC}(t)}
  \]
  (2)

  where: \( W(t) \) indoor air moisture content (kg/kg), \( W_{\text{in}(t)} \) indoor wet source moisture content (kg/s), \( W_{\text{ev}(t)} \) amount of moisture exchange between the inner surface of the enclosure and the indoor air (kg/s), \( W_{\text{f}(t)} \) amount of moisture entering the room (kg/s), \( W_{\text{HVAC}(t)} \) amount of moisture that the door and window infiltrate into the room (kg/s), \( W_{\text{HVAC}(t)} \) air conditioning humidification (kg/s).

To simulate the hygrothermal performance of the shell concrete, a simplified one-story office building was modelled as shown in Figure 4. The building has a floor area of 79 m² and a total height of 3.6 m with two uncoated double-glazed windows located at the south façade of the structure. The composition of the walls, roof, and slab are presented in the Tables 3 and 4. This composition corresponds to the composition of a BBC building that exists in the Pleiades library. Ordinary concrete will be replaced by shells concrete.

![Figure 4. Simulated structure.](image)

The initial conditions used for the Wufi simulation are presented in the table below.

The simulation has been tested for the climatic conditions of the city of Trappes (France) located in zone H1a, as shown Figure 5. In this zone, the maximum temperature difference is 4.82 °C for a winter day. On other hand, the maximum temperature difference is 2.7 °C for a summer day, with maximum energy demand of 60 kWh/m²/year.

### 2.6 Life Cycle Assessment

The goal of life cycle assessment (LCA) is to determine how damaging items are to the environment, to lessen those effects, and select goods that are least hazardous to the environment. The complete and all-encompassing evaluation of the LCA allows for
ensuring that the environmental effects brought on by potential adjustments to the building product can be compared for various scenarios, and that they are reflected in pertinent decision-making processes. For this reason, the environmental impacts of the developed material were assessed.

Table 3. The composition of the walls, roof, and slab.

| Composition       | Thickness (m) | Conductivity (W/m·K) | Density (kg/m³) | Thermal Resistance (m² K W⁻¹) |
|-------------------|---------------|-----------------------|-----------------|-------------------------------|
| **Vertical walls**|               |                       |                 |                               |
| Glass wool        | 0.2           | 0.041                 | 2               | 4.88                          |
| Concrete          | 0.2           | 1.95                  | 460             | 0.11                          |
| **Ceiling**       |               |                       |                 |                               |
| Glass wool        | 0.26          | 0.041                 | 3               | 6.34                          |
| Plaster gypsum    | 0.01          | 0.42                  | 12              | 0.02                          |
| **Slab**          |               |                       |                 |                               |
| Glass wool        | 0.2           | 0.041                 | 2               | 4.88                          |
| Concrete          | 0.2           | 1.95                  | 460             | 0.11                          |

Table 4. Hygrothermal proprieties of seashell concrete.

| Concrete         | Dry Density | Porosity | Thermal Conductivity | Specific Heat Capacity | Water Vapor Permeability |
|------------------|-------------|----------|----------------------|------------------------|--------------------------|
|                  | kg/m³       | %        | W/(m·K)              | J/(kg·K)               | Kg/(m·s·Pa)              |
| Shells concrete  | 2250        | 25 %     | 1.78                 | 920                    | 2.12 × 10⁻¹²             |

Figure 5. Map of climatic zones and Maximal energy demand [19].

An LCA approach was applied, according to the international standards of the ISO 14040 series, consisting of the following steps: (1) definition of goal and scope; (2) inventory analysis; (3) impact analysis; (4) interpretation (Figure 6).
The primary objective of this study was to determine and evaluate the environmental impacts of the shell concrete at the material scale using SimaPro tools. According to the ISO 14,040 standard, a reference functional unit must be defined for properly quantifying the environmental performance of the system. The functional unit of the present LCA study was defined to ensure the function of 1 m² for a reference life of 50 years.

For the inventory analysis, the data used in this study was gathered from several sources. Where available and applicable, the Econivent database was used. For the rest of the data, similar studies, reports, or personal communications (laboratory) were used and summarized below. The production of calcium carbonate (CaCO₃) from shells is taken from the study [20] (Table 5). The environmental indicators of calcium carbonate (CaCO₃) are used to perform a life cycle assessment at the building level using Pleiades tools. The building is occupied by four persons and heated by a gas boiler for heating.
Table 5. Inventory: Production of calcium carbonate from shells [20].

| Source                        | Quantity         |
|-------------------------------|------------------|
| Calcium Carbonate             | Shells 100 t     |
|                               | Biocide 0.7 kg   |
|                               | Diesel 57 kg     |
|                               | Water 95 t       |
|                               | Electricity 1.6 E4 kWh |
|                               | Transport 30 Tkm |
| Air emissions                 | Water 35 m³      |
|                               | Ammonia 0.2 kg   |
|                               | Particulates < 10 um 0.6 kg |
|                               | Sulfur dioxide 3 kg |
|                               | Nitrogen oxides 32.3 kg |
|                               | Carbon dioxide 1.12 kg |
| Water emissions               | COD, Chemical Oxygen Demand 8.8 kg |
|                               | BODs, Biological Oxygen Demand 0.2 kg |
|                               | Suspended solids, unspecified 1.6 kg |
|                               | Nitrogen, organic bound 0.5 kg |
|                               | Ammonia, as N 0.1 kg |
|                               | Phosphate 0.1 kg |
|                               | Nitrate 0.3 kg |
| End-of-life treatment of concrete: Concrete recycling, crushing (1 kg) | Diesel combustion 0.0143 MJ |
|                               | Electricity 0.00398 kWh |
|                               | Heat (other than natural gas) 0.00491 MJ |

3. Results and Discussion

3.1. Experimental Results

3.1.1. XRD Analysis of Scallop Powder

An XRD pattern of the scallop powder can reasonably be refined using calcite structure (Figure 7 and Table 6). The agreement factors Rwp and RB are 9.5% and 7.4%, respectively. This shows the goodness of our fit (GoF = 1.64).

Table 6. Refined values of lattice parameters, unit cell volume, average diameter, microstrain ($\langle \varepsilon^2 \rangle^{1/2}$). Standard deviations are indicated in parenthesis on the last digit.

| Phase | COD Reference | Lattice Type + Space Group | Lattice Parameters (Å) | (D) (nm) | $\langle \varepsilon^2 \rangle^{1/2}$ |
|-------|---------------|---------------------------|------------------------|----------|----------------------------------|
| Calcite (CaCO₃) | 1,547,347 | Trigonal R-3c:H | a = 4.986 (1) c = 17.070 (2) | 750 (20) | 1.10 $^{-3}$ |

3.1.2. Permeability of Mix

The addition of SS as a cement substitute slightly reduces the apparent permeability of mortar. The reduction of penetration resistance is mainly attributed to the degeneration of the pore structure. When the pore structure is finer, the penetration resistance is
improved [21]. By adding SS with high fineness, the pore structure is refined and thus the penetration resistance is enhanced (Table 7).

### Table 7. Mortar composition and permeability after 28 days.

| Sample | Mass Substitution Rate of Cement by SS (%) | Permeability after 28 Days (m·s⁻¹) |
|--------|------------------------------------------|-----------------------------------|
| CM     | 0                                        | 2.80 × 10⁻¹²                      |
| SS5    | 5                                        | 2.12 × 10⁻¹²                      |
| SS10   | 10                                       | 1.87 × 10⁻¹²                      |

3.1.3. Mortar Densities and SSA

For all mortars, an increase in the bulk density is observed with increases in the curing time from 2 up to 28 days (Figure 8a). Increasing the SS proportion led to a gradual decrease in mortar density at all curing times. This decrease is attributed to the low density of SS compared to that of the used cement. As seen in Figure 8a, the decrease is more accentuated after 2 days then after 28 days. This is due to a further densification and porosity decreases with time.

The addition of SS increases the specific surface area (SSA) of the cement powder (Figure 8b). This reduction is attributed to a larger Blaine specific surface area of SS compared to that of cement (4100 cm²/g).

- **Fresh state mortar properties**

  Our analysis shows that the substitution of cement by SS has no effect on the flow times. Indeed, all mixes present a good flow time with values close to 7 s. The water content required for the normal consistency of paste is similar for the CM and M-SS5 and decreased slightly with the incorporation of 10% of SS (Figure 9a). However, the water requirements of SS cement are comparable to those of conventional supplementary cementitious materials, such as pozzolana, fly ash, and slag [22].

---

**Figure 7.** X-ray diffraction pattern of scallop powder refined with the MAUD software.

**Table 7.** Mortar composition and permeability after 28 days.
The evolution of initial and final setting time of cement pastes with the SS ratio increase is presented in Figure 9b. The values of setting times of all paste mixes are in accordance with the NF P 15-431 standard [16]. The results show that the increase of the SS content up to 10% slightly reduced the initial setting times compared to the control paste. At the cement substitution ratio of 5%, the SS decreased the initial and final setting time by 5 min and 8 min, respectively in comparison to those of the control paste. At the cement substitution ratio of 10%, the SS decreased the initial setting time by 5 min, but the final setting time increased slightly, by 20 min. The decrease in setting time is expected and is probably due to the high finesses of SS particles, which leads to a significant increase in the number of nucleation sites, favoring the formation of more hydration products, and thus accelerating the hydration reactions [23,24]. However, an increase in the SS rate below 10% of the cement will increase the separation distance between hydrated cement particles, retard the formation of capillary bridges, and delay the formation of an interlocking network between the particles [25].

- Compressive and flexural strength of mortar

The compressive and flexural strength values of elaborated mortars after 2, 7, 14, and 28 curing days are presented in Figure 10. Regardless of the considered formulation, the mortar’s compressive strength increases with time. The results show also that only the 5% cement replacement by SS produced higher strength for all curing times. Indeed, the compressive and flexural strengths for the M-SS5 mortar increase, and surpass the control mortar at 28 days, by 6.6%. The maximum compressive strength at 28 days is
then obtained with 5% SS replacement with a value of 60.45 MPa. Above 10% of SS substitution, the compressive strength decreases with the replacement rate and is greater than 50 MPa. However, the results obtained for the cement mortar mixes with 10% of SS are still acceptable for application in the construction industry.

![Figure 10](image)

**Figure 10.** Average compressive and flexural tensile strengths at different ages of the mixtures with SS additions.

Generally, only certain mixtures with calcium carbonates systems (such as limestone and SS) resulted in high compressive strength compared to the CM. The decrease in strength at high levels of replacement is probably due to the high finesses of SS compared to cement, and the subsequent aggregation of SS particles at high proportions. The aggregation of SS particles will destabilize the system by preventing the formation of homogeneous hydrated microstructures, and thus leading to a strength decrease [26].

If the content of shells and the distance between the SS particles are appropriate, the CSH hydration will be suitably controlled, limiting the growth of portlandite. In addition, the high fineness of SS particles in mortar promotes the hydration of cement due to their high activity and the dissolution of calcium present at high proportions.

After 28 days of age, Raman examinations of the control mortar surface (Figure 11) reveal the presence of C-S-H.

There has been extensive research on the Raman spectra of the C-S-H systems [27,28]. Si-O stretching is responsible for the band with the highest intensity at 680 cm\(^{-1}\). A contribution at 445 cm\(^{-1}\) is attributed to the twisting and stretching of the Si-O-Si bounds, and bands in the range of 950 to 1100 cm\(^{-1}\) are connected to the symmetric stretching modes of Q\(_n\) species in silicates (Si-O). These bands are present in the low wavenumber range (100–360 cm\(^{-1}\)) and are attributed to the lattice vibrations of Ca-O polyhedra. When the Raman spectra of C-S-H formed on non-substituted mortars and SS5-SS10 are compared, there is a significant increase in intensity and decrease in bandwiths of the vibrational modes (lattice vibrations of Ca-O polyhedral) as a function of seashell content increase. This phenomenon is due to the addition of scallop shells, which lead to an increase in the ordering of the calcium environment, resulting in a higher degree of polymerization.
The amounts of ettringite and calcium carboaluminate in the mixtures increased as the processes, particularly those involving the aluminate phases, resulting in the development of ettringite and the precipitation of hydration products (C-S-H). The effectiveness of seashells was attributed to the liberation of CO$_3^{2-}$ ions, which led to the formation of carboaluminates and the reduction of concrete porosity, which increased flexural and compressive strengths. Wang et al. demonstrated that the water absorption of concrete increases with CaCO$_3$ content, and that concrete with a higher cockle shell ash content is more porous [30].

- **Thermal conductivity of seashell concrete**

As can be seen from Table 8, thermal conductivity of the formulated control concrete is 1.95 W·m$^{-1}$·K$^{-1}$. For the specimen M-SS10, the value of thermal conductivity is 1.78 W·m$^{-1}$·K$^{-1}$. These results show that the addition of SS slightly improves the thermal conductivity of the concrete. Indeed, the use of 10% of SS decreased the thermal conductivity by 9% at 20 °C in comparison with standard concrete.

**Table 8.** Variation of the thermal conductivity, porosity, and density of the concretes elaborated with different proportions of SS after 28 days of curing. Standard deviations are calculated for 3 replicates.

| Sample | Porosity | Density (g·cm$^{-3}$) | Thermal Conductivity (W·m$^{-1}$·K$^{-1}$) |
|--------|----------|-----------------------|-------------------------------------------|
| CM     | 32%      | 2.37± 0.5             | 1.95 ± 0.03                               |
| SS5    | 28%      | 2.28 ± 0.5            | 1.86 ± 0.02                               |
| SS10   | 25%      | 2.25 ± 0.5            | 1.78 ± 0.02                               |

- **Life cycle analysis**

The environmental impact results of shell concrete production are presented in Figure 9 for 1 m$^2$ using SimaPro tools. The impact results are presented as a percentage of the...
greatest impact in each category. The results show that the cement and sand materials stand out as the largest contributors to the environmental impacts. For 10% of cement substruction by shells, cement has an impact of 80% for the indicator “Climate change” (Figure 12a). Furthermore, the shells generate a maximum rate of 41% for the indicator “Marine eutrophication”. This seems to indicate that including 10% shells represents a decrease of up to 40% of the environmental impact, depending on the category of impact considered (Figure 12b).

Figure 12. Environmental impact. (a) Distribution of raw material impacts and (b) Cement impact.

To identify the elements of the life cycle of a building (Figure 3) based on shell concrete (10%), a contribution analysis has been carried out using Pleiades software, as shown Figure 13. This analysis focuses on 33 impact indicators representative of the sum of the four phases of a building’s life cycle (construction, use, renovation, and demolition). The simulation was made for a life cycle based on four occupants. The results show that the construction and renovation phases are the most important. This finding confirms the results obtained by Lotteau et al. [31] who showed that the utilization phase of the building produces the most important environmental impacts in terms of quantity.

Therefore, we focused particularly on the greenhouse effect, as shown Figure 14. Given the importance of the use and retrofit phases, it is interesting to determine which assumptions lead to this difference. The results show that the heating is the most impactful element. The use of a gas boiler has a significant impact on the environment, because of its lifespan, and has a very important impact on all the indicators. It is considered that DHW (Domestic Hot Water) tanks and HVAC systems (Heating, Ventilation, and Air-Conditioning) should be replaced every 20 years. The renovation phase consists mainly of the renewal of windows and internal walls.

- Hygrothermal behavior

The building is located in Trappes, France, which has a humid climate with mean values of temperature and humidity of 14 °C and 75%, respectively. The weather data used in this work was obtained from the database embedded in the WUFI® Plus program, which is shown in Figure 15.
For the simulation, it is assumed that the building has four occupants. In this study, we are interested in hygrothermal comfort, as shown in Figure 16, without mechanical cooling/heating systems. As shown in Figure 16a, a high indoor relative humidity has been observed which can negatively influence human health. For some time periods, the optimal thermal comfort was not ensured, and circles move outside of the optimal thermal comfort region due to the higher relative humidity. A good level of comfort can also be found in other periods. The variation of humidity inside the building is influenced by the occupants and the porosity of the wall. For this purpose, in Figure 16b we present the variation of inner moisture source (occupants) and moisture exchange with partitions. The results in Figure 16b show that the wall can provide, or release moisture generated by

Figure 13. Impacts distribution according to life stage.

Figure 14. Greenhouse effect for the use and retrofit phases.
the occupants. Positive values represent moisture added to the zone and negative values represent moisture leaving the zone.

Figure 15. Climatic conditions.

Figure 16. (a) Hygrothermal comfort and (b) moisture flow.
4. Conclusions

This paper presents the effects of cement substitution by scallop shells at different levels. The hygrothermal and mechanical characterizations of the scallop shell concrete sample as well as the numerical analysis accompanied by LCA yield some promising findings, which may be summarized as follows:

- The replacement of cement by up to 10 wt.% of scallop shells does not significantly affect mortar properties.
- The greater effectiveness of scallop shells is attributed to their higher calcium content and the high finesses of SS particles in mortar, which promote the hydration of cement due to their high activity and the dissolution of calcium present at high proportion in scallop shells.
- A real potential for the use of scallop shells by-products as partial replacement for cement, at an optimum rate of 10% is evidenced.
- This new material is a good candidate to extensively contribute to the achievement of sustainable development goals and carbon emission reduction. Indeed, the results indicate that cement substitution by 10% shells in concrete represents a decrease up to 40% of the environmental impact.
- The results found using Wufi, show that the wall ensures a hygroscopic exchange which allows the evacuation of the humidity generated by the occupants.

These initial findings highlight the need for further complementary investigations. Indeed, this work presents some limitations:

- With regard to thermal properties, thermal conductivity and thermal diffusivity has been studied; nevertheless, mass loss via a differential scanning calorimeter and thermo-gravimetric analysis is necessary to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition or oxidation. XRD analysis will also be necessary to understand the effect of the addition of carbonates on the mineralogical composition of the concrete, and thus to understand the hydration mechanism of the cement.
- The shear behavior here is one of the properties to be studied in the future as fracture in a material is often due to shear.

Author Contributions: Conceptualization, Y.E.M. and M.-H.B., methodology, Y.E.M. and M.-H.B., software, Y.E.M. and M.-H.B., validation, Y.E.M. and M.-H.B., analysis Y.E.M. and M.-H.B., investigation, Y.E.M. and M.-H.B., data curation, Y.E.M. and M.-H.B., writing—original draft preparation, Y.E.M. and M.-H.B., writing—review and editing, Y.E.M. and M.-H.B., visualization, Y.E.M. and M.-H.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research is supported by the European Regional Development Fund for having sponsored this study within the framework of a BLUEPRINT to a Circular Economy project (Interreg V A France (Channel) England, Project n°206).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This research is associated with the national DD&RS strategy (Sustainable Development and Social Responsibility, ‘développement durable et responsabilité sociale’ in French).

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

1. United Nations et Department of Economic and Social Affairs, Energy Statistics Pocketbook, United Nation, OSBN-10 9212591485, San Francisco, CA, USA. 2020. Available online: https://unstats.un.org/unsd/energystats/pubs/documents/2020/lp-b-web.pdf (accessed on 12 June 2022).

2. Bouasria, M.; Khadraoui, F.; Benzaama, M.-H.; Touati, K.; Chateigner, D.; Gascoïn, S.; Pralong, V.; Orberger, B.; Babouri, L.; Mendili, Y.E. Partial substitution of cement by the association of Ferronickel slags and Crepidula fornica shells. J. Build. Eng. 2021, 33, 101587. [CrossRef]

3. Mosher, S.; Cope, G.W.; Weber, F.X.; Shea, D.; Kwak, T.J. Effects of lead on Na+, K+-ATPase and hemolymph ion concentrations in the freshwater mussel Elliptio complanata. Environ. Toxicol. 2012, 27, 268–276. [CrossRef] [PubMed]

4. Bouasria, M.; Benzaama, M.H.; Pralong, V.; El Mendili, Y. Mechanical and hygrothermal performance of fly-ash and seashells concrete: In situ experimental study and smart hygrothermal modeling for Normandy climate conditions. Archives. Civil. Mechan. Eng. 2022, 22, 100. [CrossRef]

5. Varhen, C.; Carrillo, S.; Ruiz, G. Experimental investigation of peruvian scallop used as fine aggregate in concrete. Constr. Build. Mater. 2017, 136, 533–540. [CrossRef]

6. Neamitha, M.; Muthadhi, A. Performance of pervious concrete with industrial waste as coarse aggregate e a new overview. Int. J. Emerg. Technol. Adv. Eng. 2016, 6, 155–161.

7. Nor Hazurina, O.A.B.; Megat Johari, B.H.; MA Mat Don, M. Potential use of cockle (anadara granosa) shell ash as partial cement replacement in concrete. Casp. J. Appl. Sci. Res. 2013, 2, 369–376.

8. Bassam, A.T.; Mohammed, W.H.; Zeyad, A.M.; Yusuf, M.O. Properties of concrete containing recycled seashells as cement partial replacement: A review. J. Clean. Prod. 2019, 237, 117723.

9. Othman, N.H.; Bakar, B.H.A.; Don, M.; Johari, M. Cockle shell ash replacement for cement and filler in concrete. Malays. J. Civil. Eng. 2013, 25, 201–211. [CrossRef]

10. Cao, S.; Li, X.; Yang, B. Heat and moisture transfer of building envelopes under dynamic and steady-state operation mode of indoor air conditioning. J. Build. Eng. 2021, 44, 102683. [CrossRef]

11. Jiang, S.S.S.; Hao, J.L.; de Carli, J.N. Hygrothermal and mechanical performance of sustainable concrete: A simulated comparison of mix designs. J. Build. Eng. 2021, 34, 101859. [CrossRef]

12. Grazulis, S.; Daškevič, A.; Merkys, A.; Chatéigner, D.; Lutterotti, L.; Quiros, M.; Serebyryanaya, N.R.; Mocek, P.; Downs, R.T.; Le Bail, A. Crystallography Open Database (COD): An open-access collection of crystal structures and platform for world-wide collaborative. Nucleic. Acids. Res. 2012, 40, D420–D427. [CrossRef] [PubMed]

13. Lutterotti, L.; Matthies, S.; Wenk, H.R.; Schultz, A.S.; Richardson, J.W. Combined texture and structure analysis of deformed limestone from time-of-flight neutron diffraction spectra. J. Appl. Phys. 1997, 81, 594–600. [CrossRef]

14. ASTM C204-18ε1; Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus. ASTM International: West Conshohocken, PA, USA, 2018.

15. NF P18-452, February 2017; Concretes-Measuring the flow time of concretes and mortars using a workabilitymeter. AFNOR: Paris, France, 2017.

16. NF P 15-431. Février 1994. P 15-431; Liants Hydrauliques-Technique Des Essais-Determination Du Temps De Prise Sur Mortier Normal. AFNOR: Paris, France, 1994.

17. NF EN 196-1; Méthodes D’essais Des Ciments-Partie 1: Détérioration Des Resistances-Méthodes D’essais Des Ciments. AFNOR: Paris, France, 2016.

18. Wuffi, Fraunhofer, Munich, Germany. Available online: https://wufi.de/en/software/wufi-plus/ (accessed on 12 June 2022).

19. Gounni, A.; Louahlia, H. Dynamic behavior and economic analysis of sustainable building integrating cob and phase change materials. Constr. Build. Mater. 2020, 262, 120795. [CrossRef]

20. Iribarren, D.; Moreira, M.T.; Feijoo, G. Implementing by-product management into the Life Cycle Assessment of the mussel sector. Resour. Conserv. Recycl. 2010, 54, 1219–1230. [CrossRef]

21. Zhang, M.H.; Li, H. Pore structure and chloride permeability of concrete containing nano-particles for pavement. Constr. Build. Mater. 2011, 25, 608–616. [CrossRef]

22. Sobolev, K.; Kozhukhova, M.; Sideris, K.; Menéndez, E.; Santhanam, M. Properties of Fresh and Hardened Concrete Containing Supplementary Cementitious Materials: State-of-the-Art Report of the RILEM Technical Committee 238-SCM Working Group 4; Alternative Supplementary Cementitious Materials: Springer International Publishing: Cham, Switzerland, 2018; Volume 25, pp. 233–282.

23. Gutteridge, W.; Dalziel, J. Filler cement: The effect of the secondary component on the hydration of Portland cement: Part 2: Fine hydraulic binders. Cem. Concr. Res. 1990, 20, 853–861. [CrossRef]

24. Marzouki, A.; Lecomte, A.; Beddey, A.; Diliberto, C.; Ouezdou, M.B. The effect of grinding on the properties of Portland-limestone cement. Const. Build. Mater. 2013, 48, 1145–1155. [CrossRef]

25. Matschei, T.; Lothenbach, B.; Glasser, F.P. The Role of Calcium Carbonate in Cement Hydration. Cem. Concr. Res. 2007, 37, 551–558. [CrossRef]

26. Li, G. Properties of High-Volume Fly Ash Concrete Incorporating Nano-SiO2. Cem. Concr. Res. 2004, 34, 1043–1049. [CrossRef]

27. Kirkpatrick, R.J.; Yarger, J.L.; McMillan, P.F.; Yu, P.; Cong, X. Raman spectroscopy of C-S-H, tobermorite, and jennite. Adv. Cem. Based Mater. 1997, 5, 93–99. [CrossRef]
28. Garbev, K.; Stemmermann, P.; Black, L.; Breen, C.; Yarwood, J.; Gasharova, B. Structural features of C-S-H(I) and its carbonation in air- A Raman spectroscopic study. Part I: Fresh phases. J. Am. Ceram. Soc. 2007, 90, 900–907. [CrossRef]

29. Mohammad, W.A.S.B.W.; Othman, N.H.; Ibrahim, M.H.W.; Rahim, M.A.; Shahidan, S.; Rahman, R.A. A review on seashells ash as partial cement replacement. IOP Conf. Ser. Mater. Sci. Eng. 2017, 271, 012059. [CrossRef]

30. Wang, Z.; Chen, Y. Data-driven modeling of building thermal dynamics: Methodology and state of the art. Energy Build. 2019, 203, 109405. [CrossRef]

31. Lotteau, M.; Loubet, P.; Pousse, M.; Dufrasnes, E.; Sonnemann, G. Critical review of life cycle assessment (LCA) for the built environment at the neighborhood scale. Build. Env. 2015, 93, 165–178. [CrossRef]