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Recycling Bio-Based Wastes into Road-Base Binder: Mechanical, Leaching, and Radiological Implications

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Abstract: This work presents a physical, mechanical, durability, leaching, and radiological assay of three wastes (egg and scallop shells and olive pomace ash) as road-base binders. Two different waste/Portland-cement ratios (7.5/92.5 and 80/20) were studied. Density and compressive strength decreased when different wastes were added in every proportion. Additions of 7.5% of both shells reduce the density to about 2.5% and the compressive strength to 20%, while 80% reduces the density to 20% and the compressive strength to 90%, while the addition of biomass fly ash decreases the density and compressive strength in a higher proportion than shells. The durability against acid attack is increased when the three wastes are used, and this increase is higher when the waste dosage is increased (up to 15 times more when 80% biomass ash is used). With respect to leaching, scallop and eggshells can be used as a component of hydraulic road binder, but olive pomace ash presents leaching values higher than the limits of different regulations (Se, Pb, Ni, Mo, Cu, and As). From a radiological perspective, all road-base binders present an activity concentration index lower than 1, except when olive pomace ash was used, and the binders showed higher values of ^{40}K due to the high potassium content of fly ash.

Keywords: scallop shell; eggshell; olive pomace ash; leaching; radioactivity; road-base binder

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1. Introduction

A road-base binder is a powder, made of a mix of different components, which is the basis for constructing hydraulically bound base mixtures for the treatment of materials for bases, sub-bases and capping layers, and earthworks in airports, roads, railways, and other infrastructures [1]. Portland cement, bituminous materials, lime, and industrial wastes such as slag, furnace dust, coal fly ash, and others (up to 10% by mass) are the most common materials used in road binders [2]. Although there is potential for the use of waste materials and the reduced consumption of high-value components such as cement [1], there are few investigations related to the incorporation of waste in road binders [2], especially the environmental (heavy metals and radioisotopes) assessment of the waste incorporated. Mainly, the incorporation of waste in hydraulic road binders has focused on wood ash [3], cellulose ash [2], and steel slag [4]. Therefore, at present, the technical and environmental feasibility of incorporating other wastes composed mainly of limestone, such as seashells and eggshells, is unknown. No previous studies have been extended to other types of ash, such as olive pomace ash.

European standards EN 13282-2 [5] on additives to road-base binders indicate the characteristics that certain wastes must have to be used in this kind of application. One of them is that the waste cannot emit radiation or contain hazardous materials. Even so, the standards do not always specify the tests that must be performed or the maximum limits that cannot be exceeded, and that is what this study attempts to investigate in depth. Globally, population growth has caused an increase in the demand for manufactured food and, therefore, an increase in waste generation [6]. On the other hand, worldwide, construction demands more natural resources than any other sector [7]. To improve the environmental sustainability of construction and other sectors, different wastes, some of a biological nature, have been evaluated as substitutes for materials traditionally used in construction (cement, mortar, and concrete) [8].

For example, the global aquaculture industry produces between six and eight million tons per year of seashells from different sources (scallops, oysters, mussels, cockles, etc.) [9]. Approximately 60% of total production becomes waste [10] and only 25% of this is reused [11]. Furthermore, the disposal of seashell waste generates unpleasant odors and requires a large area of land for dumping [12]. The same environmental problems occur in the poultry industry, which generates more than 250,000 tons of eggshell waste per year [13]. Other biological wastes are generated in the agricultural sector, such as olive pomace. It is estimated that a ton of processed olives produces approximately 27% olive oil and 73% waste. In Andalusia (Spain) alone, three million tons/year of pomace are generated [14]. The improper management of olive pomace can cause major environmental problems due to its high phenol content [15].

Eggshells are useful in various construction materials, such as cement [16], mortar, concretes, alkali-activated binders, and bricks [17] (due to their high calcium carbonate content. Eggshell powder has shown good strength parameters when mixed with concrete, from previous studies shown below [18]. There are previous studies on the use of seashell waste in cement production [19], as a fine/coarse aggregate in concrete [20–22], and as fireproof materials [11].

Due to its high energy content and low fuel cost, olive pomace is used as biomass; approximately 30% is used to produce electric energy. However, the combustion of olive pomace produces more than 50,000 tons/year of ash [14]. These ashes have been used in cement manufacturing [23], bricks [24], fireproof materials [25], geopolymers [14,26], and mortar [27].

In this study, three different wastes of biological origins (eggshells, seashells from scallops, and ashes from biomass combustion (olive oil pomace)), have been used as raw materials in road binder.

Although these three wastes are biological in origin, previous studies have declared the presence of heavy metals in eggshells [28,29] and seashells [30]. Olive oil pomace ash contains heavy metals (such as As and Pb) and a high content of potassium [25]. Therefore, these wastes could contain leachable heavy metals and radioisotopes, which, although present in low concentrations in the waste, make their use as construction materials unviable due to health and environmental risks.

The research significance of this study is to assess and compare the physical, mechanical, and environmental properties of road binders when part of the cement is replaced by different bio-wastes (fly ash from olive pomace, eggshells, and seashells) into road binders in different proportions.

2. Materials and Methods

2.1. Tested Materials

Portland cement (CP) type II 32.5 N according to European standards [31] was used. The cement particle size was less than 90 µm Three different wastes have been analyzed: (1) Chilean–Peruvian scallop shells (Argopecten purpuritas) (SC) from the Chilean aquaculture industry were used. The material was previously crushed to obtain a particle size lower than 350 µm. (2) Eggshell (E) was generated as solid waste generated from bakeries and was previously crushed to a particle size of less than 350 µm. (3) Fly ash (OR) from olive pomace combustion in a power plant in southern Spain was used. The ash was sieved to obtain a maximum particle size of 350 µm. The particle size distribution is shown in

Figure 1. It was measured by using a Saturn DigiSizer II model. Egg and scallop shells present the highest differential percentages between 50 and 250 µm and are similar for all the sizes of this interval, The average particle size of scallop shells is 98 µm, as shown in Figure 1. Eggshells present a medium value (85 µm) slightly lower than scallop shells. Fly ash from olive pomace combustion presents the highest differential percentages in the range between 20 and 150 µm with a medium particle size of 44 µm, but all of them are higher than Portland cement.

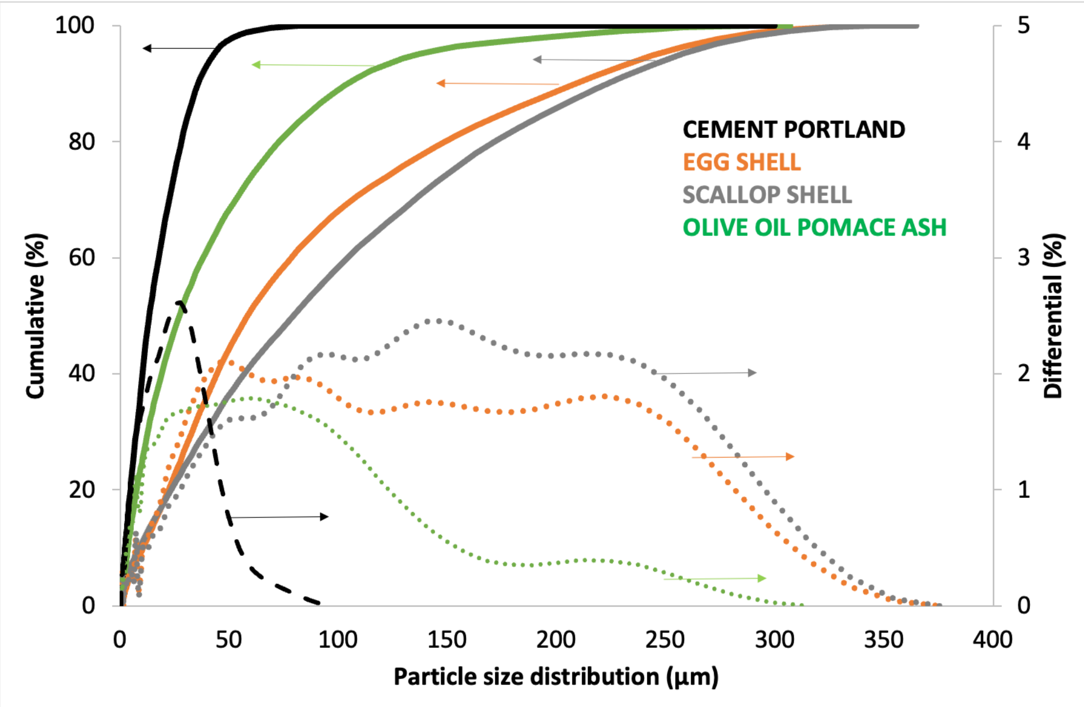

Figure 1. Particle size distribution of scallop shells, eggshells, and fly ash from olive pomace combustion.

The chemical composition of the materials was determined after chemical attack and dissolution at 750 °C (ASTM D 3682 [32]) using atomic absorption spectroscopy. Table 1 shows the main chemical components; the composition is expressed as oxides (but this does not imply that they are present in the material as oxides, either before or after calcination). The specific density was obtained according to ASTM D 854 [33].

As shown in Table 1, the main component in the shells of eggs (E) and scallops (SC) was calcium carbonate [11–13]. The calcium carbonate decomposes at a temperature between 650 and 700 °C, so when analyzed after its calcination, CaO appears and the LOI collects, which corresponds to CO_2 decomposed during the previous calcination. Additionally, the eggshells presented a little more SiO_2, Fe_2O_3, and SO_3. However, the scallop shells presented a greater amount of Na because, unlike eggshells, they are in contact with seawater. Olive oil pomace ash is mainly composed of silica and potassium, and the LOI value is due to the unburned matter present in the ash. According to EN 13282-2 [5], all wastes complied with the permitted concentration of SO3: less than 4%.

The specific gravities of these wastes are lower than those of Portland cement (CP). Both types of shells present a similar specific density because they have a similar chemical composition.

Table 1. Main chemical components (% weight) of Portland cement, scallop shells, eggshells, and olive oil pomace ash. Note: CP: Portland cement; SC: scallop shells; E: eggshell; OR: fly ashes; LOI: loss on ignition.

	CP	**SC**	**E**	**OR**
SiO_2 (%)	13.8	0.01	0.6	26.8
Al_2O_3 (%)	3.5	0.04	0.07	6.8
Fe_2O_3(%)	2.3	-	0.6	5.2
MnO (%)	0.1	0.04	-	5.6
MgO (%)	0.7	-	0.4	5.1
CaO (%)	59.3	54.0	62.4	16.4
Na_2O (%)	0.1	0.5	-	1.5
K_2O (%)	0.5	-	0.2	22.5
TiO_2 (%)	0.2	-	-	-
P_2O_5 (%)	0.1	0.1	-	-
SO_3 (%)	1.7	0.3	1.3	-
LOI (%)	15.5	43.2	34.4	9.4
Specific Density (g/cm^3)	3.19	2.63	2.64	2.73

2.2. Specimen Manufacturing Method

Although additives greater than 10% are not recommended according to EN 13282-2 [5], 7.5 and 80% replacements were carried out to obtain significant differences in the radiological study, keeping the water/solid ratio constant and equal to 0.35. The different compositions are shown in Table 2.

Table 2. Tested compositions. Note CP: Portland cement; SC: scallop shells; E: eggshell; OR: biomass fly ash.

Composition	**Cement (%)**	**Waste (%)**	**Water/Solid Ratio**
CP-100	100	-	0.35
CP-92.5-SC-7.5	92.5	7.5	
CP-20-SC-80	20	80	
CP-92.5-E-7.5	92.5	7.5	
CP-20-E-80	20	80	
CP-92.5-OR-7.5	92.5	7.5	
CP-20-OR-80	20	80	

Cement and waste were mixed for 4 min until a homogeneous mixture was obtained, for all the different compositions. After adding water to the mixture and mixing for 5 min, a workable mixture was obtained. Cylinder molds were filled once the mixture had reached the proper consistency. After 24 h, the material was demolded, then cured for another 27 days at 20 °C and 60% relative humidity.

2.3. Physical and Mechanical Properties

The density was calculated in accordance with EN 1936 [34]. The compressive strength (CS) of the test specimens was determined based on the EN 196-1 [35] using a compression test machine (Tinus-Olsen). These tests were carried out on 4 × 4 × 4 cm prismatic specimens. Each result was obtained by testing three specimens.

2.4. Durability: Resistance to Acid Attack

In many applications under severe environmental conditions, the choice of a binder influenced the durability of finished materials, and in this work, mechanical resistance under a chemical attack (acid) has been studied.

The resistance to acid attack (RA) of the hydraulic road binder has been measured according to previous studies [36]. After a 28-day curing period, some samples were immersed in water (reference specimens) and others in a 1 M sulfuric acid solution for 14 days. Three samples in water and three in acid have been tested for each composition. The compressive strength of the attacked specimens was measured (CS-acid) and reference specimens (CS-water) were compared according to the equation:

$$RA = \frac{CS - acid}{CS - water} \quad (1)$$

2.5. Environmental Study

European standards EN 13282-2 [5] indicate the characteristics that some wastes should meet to be used in road-base binders. One of them is that waste should not contain dangerous leaching substances or emit radiation.

2.5.1. Leaching Study

The most common leaching test in Europe is EN-12457-4 [37], and it is used to classify wastes according to the EU Landfill Directive [38]. The test is very simple. For materials with particle size distributions less than 10 mm, it is based on single-stage leaching at a liquid/solid ratio of 10/1. The mixed liquid/solid was rotated for 24 h at 15 rpm. Deionized water was used in this study. An ICP spectrometer (Agilent Technologies, Madrid, Spain) from the Research, Technology, and Innovation Center at the University of Seville (CITIUS) was used. Two leaching tests for each leaching were carried out.

In addition, this test is used in some European national and regional leaching regulations in order to assess the use of waste in construction applications. For instance, Portugal [39], Italy [40], and some regions of Spain (Catalonia [41] and Basque Country [42]) have established leaching limits according to this test's results for the valorization of wastes as construction materials Metal analysis in leachates have been carried out through the Inductively Coupled Plasma technique.

2.5.2. Radiological Study

Radioactive nuclides are found in varying amounts in traditional building materials and wastes [43]. Natural building materials and wastes contain various amounts of natural radioactive nuclides [43]. Many wastes could be considered NORM (naturally occurring radioactive material) [44], and their use is subject to the legal restrictions of international radiation protection safety standards, such as the European Directive 2013/59 [45]. These standards establish several parameters to characterize the final construction material containing wastes: activity concentration index (I), the absorbed dose (D, Gy/h), radium activity (Ra_{eq}), and effective dose (E, Sv/y). All these parameters are obtained by their activity concentration (in Bq/kg) of ^{232}Th and ^{238}U series radionuclides, and ^{40}K, which can be determined by gamma-ray spectrometry [8].

Two samples were tested for each composition. Cylinder specimens were positioned directly at the top of the detector endcap. A Canberra low-background high-purity germanium GR-6022 reverse electrode coaxial (XtRa) detector (60% relative efficiency) shielded by a 10 cm-thick high-purity lead served as the primary detector. The detector was connected to a DSA-1000 digital spectrum analyzer. The spectra were analyzed using Canberra Genie 2000 gamma software (version 3.2). All the samples were related to one day of sampling. The activity concentrations of the different gamma emitters were determined through the energies of ^{232}Th (911.2 keV of ^{228}Ac), ^{238}U (or its daughter ^{226}Ra via 351 keV emissions of ^{214}Pb), and ^{40}K (1460 keV).

Additionally, a Low Energy Germanium (LEGe) GL-2020 detector was used for checking performance at low and moderate energies because it was fabricated with a thin side and front contact affording a better resolution than any other detector. The LEGe detector had an active area of 2000 mm^2 and thickness of 20 mm, and a 0.6 mm carbon epoxy window that improves ruggedness while maintaining good low-energy transmission was used.

The detectors' absolute efficiencies were calculated using Canberra LabSOCS software, which is based on the MCNP Monte Carlo code, considering the self-absorption of low-energy gamma rays within the sample [46]. The minimum detectable activity (MDA) and the decision level of both detectors for ^{40}K, ^{210}Pb, ^{238}U, and ^{232}Th were calculated according to ISO 11929-4 [47]. Additionally, an alternative geometry was checked by placing a cylinder specimen viewed from the side (see Figure 2). The MDA values for this measuring geometry were compared with the geometry of a cylinder specimen viewed from the top.

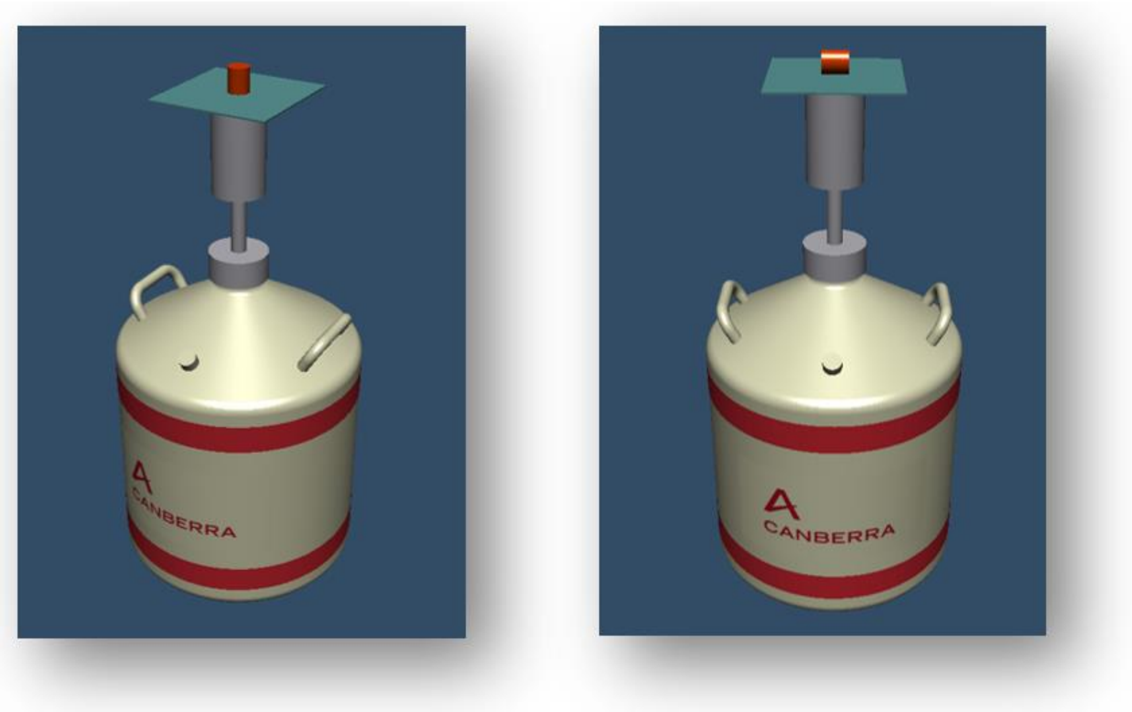

Figure 2. Gamma-ray spectrometry setup showing the measuring geometries with a cylinder specimen viewed from the top (**left**), and a cylinder specimen viewed from the side (**right**).

Finally, the gamma-ray spectrometry analyses were validated based on several inter-comparison programs [46,48].

The gamma radiation dose was calculated to assess the radiological hazard of the proposed hydraulic binders. Activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K were converted into the absorbed gamma dose rate (D) using the conversion factors presented in the literature [49] at 1 m above ground (in mGy/h by Bq/kg):

$$D\left(\frac{nG}{h}\right) = 0.462 \cdot a_{Ra-226} + 0.604 \cdot a_{Th-232} + 0.147 \cdot a_{k-40} \quad (2)$$

Then, D can be converted into the annual effective dose indoors (E) according to Equation (3):

$$E\left(\frac{mSv}{y}\right) = 0.8 \cdot 10^{-6} \cdot Q \cdot D \cdot T \quad (3)$$

where (1) Q is a converting value of 0.7 Sv/Gy for gamma-ray environmental exposure; (2) the indoor occupancy factor of 0.8 indicates that 80% of the time was spent indoors; and (3) T is the time, equal to 1 year (8760 h.) [49].

On the other hand, the activity concentration index (I) is defined as:

$$I = \frac{a_{Ra-226}}{300} + \frac{a_{Th-232}}{200} + \frac{a_{K-40}}{3000} \quad (4)$$

where a_x is the activity concentration of nuclide x in the construction material analyzed (Bq/kg).

According to the European Commission Radiation Protection 112 technical guide [50], it was developed as a tool for screening construction materials.

"I" gives an assessment of the gamma radiation dose that an individual may receive from construction materials. For bulk materials, if I $\leq$ 1.0; E is $\leq$1 mSv/y and the material could be used safely from a radiological point of view.

Finally, radium activity (Ra_{eq}) determines the radiological hazards of ^{232}Th, ^{226}Ra, and ^{40}K distributed in construction materials. Ra_{eq} is a weighted sum of the activity concentrations of the radionuclides considering that 259 Bq/kg of ^{232}Th and 4810 Bq/kg of ^{40}K cause the same gamma dose due to 370 Bq/kg of ^{226}Ra [51].

$$Ra_{eq} = (a_{Ra-226}) + (1.43 \cdot a_{Th-232} + 0.077 \cdot a_{K-40}) \quad (5)$$

where a_x is the nuclide x activity concentration (Bq/kg).

A safe construction material produces an external dose below 1.5 mGy/y, corresponding to a Ra_{eq} value lower than 370 Bq/kg.

JASP R-based statistical software (version 0.14.1) was used for statistical analysis. Pearson's correlation was calculated to consider the relationships between the physicochemical properties, radioactivity concentrations, and radiological parameters. Positive correlations are shown in blue, while negative correlations are shown in red on a correlation heat map. Correlations with p-values greater than 0.01 were considered insignificant, correlations with p-values less than 0.05 implied a 5% probability of random chance, p-values less than 0.01 implied a 1% probability, and p-values less than 0.001 implied a 0.1% probability of random chance.

3. Results and Discussion

3.1. Physico-Mechanical Properties of Road-Base Binder

The density and CS of road-base binders decrease when different wastes are added in any dosage, as shown in Table 3. The density was reduced because 1) wastes present a higher particle size distribution than cement, which increases porosity between particles, and 2) wastes have lower specific gravity than cement and, consequently, a higher porosity within the particles (see Table 1). In this study, the specific gravity and particle size distribution of the egg and scallop shells are similar, producing densities very similar. When OR is used, the particle size is lower than both shells, and the specific gravity is like the other two wastes, producing a denser material.

Also, the CS decreased when all wastes were added and when the proportion was increased. From a physical point of view, egg and scallop shells present a similar density, and, therefore, they have similar porosities, but they are higher than only Portland cement binders (CP-100). From a chemical point of view, scallop and eggshells are principally calcium carbonate and, therefore, they are an inactive addition because they do not have pozzolanic properties [52]. Both effects diminish the compressive strength when both wastes are added at a similar level. When OR is added, the compressive strength is reduced more than the shells' addition due to the low reactivity of this kind of ash and because when OR is added, the compressive strength is reduced more than shells' addition, due to the low reactivity of OR and because the number of principal hydration outputs of cement such as C-S-H and $Ca(OH)_2$ are diminished [53].

Regardless of the type of waste, the compositions made with 7.5% waste and CP meet the minimum mechanical requirements to be used as normal hardening road-base binders according to EN 13282-2 2. CP-92.5-OR-7.5 and CP-92.5-E-7.5 could be classified as N2 (compressive strength between 12.5 and 32.5 MPa), while CP-92.5-SC-7.5 and CP could be classified as N4 (compressive strength between 32.5 and 52.5 MPa). If the compressive strength is compared with road binder containing waste-paper ash in a similar dosage [54], the compressive strength is higher in the three wastes analyzed in this work, but lower when steel slag is used [55].

Table 3. Physical and mechanical properties Note: CP: Portland cement; SC: scallop shells; E: eggshell; OR: biomass fly ash.

Composition	Density (kg/m^3)	CS (MPa)
CP-100	1857 ± 22	42.6 ± 1.2
CP-92.5-SC-7.5	1813 ± 21	37.8 ± 1.3
CP-20-SC-80	1449 ± 17	2.5 ± 0.3
CP-92.5-E-7.5	1800 ± 25	33.2 ± 0.9
CP-20-E-80	1507 ± 18	2.6 ± 0.3
CP-92.5-OR-7.5	1846 ± 19	23.3 ± 0.8
CP-20-OR-80	1651 ± 11	1.4 ± 0.2

3.2. Durability: Acid Resistance of Roa- Base Binders

As shown in Figure 3, when the amount of waste in the binder is increased, the acid attack coefficient increases. For specimens CP-20-OR-80, CP-20-SC-80, and CP-20-E-80, the acid attack coefficient is greater than 1. Part of the Ca present in waste and cement in an acidic environment dissolves in water so that Ca^{2+} reacts with SO_4^{2-}, producing $CaSO_4 \cdot 2H_2O$. As shown in Figure 4, the acid attack caused the generation of a gypsum layer on the surface and inside the specimen, giving the specimens a white appearance. This formed gypsum has a higher compressive strength than the material before the acid attack [56]), so in cases of high waste dosage, it increases compression resistance. However, in materials with higher initial compressive strength and lower porosity (higher density), the gypsum induces higher volumetric expansions and leads to the spalling of the surface layers, producing a diminution after the attack [57].

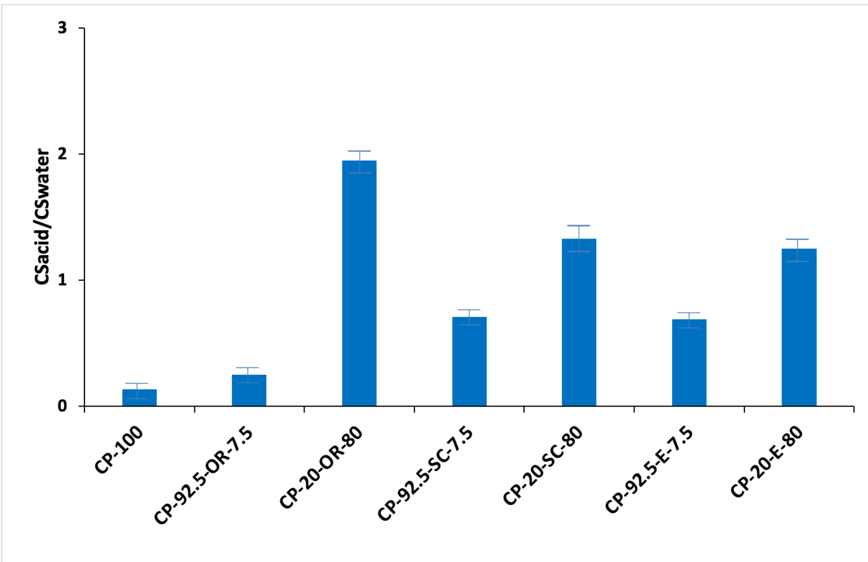

Figure 3. Resistance to the acid attack of hydraulic road binders. Note: CP: Portland cement; SC: scallop shells; E: eggshell; OR: biomass fly ash.

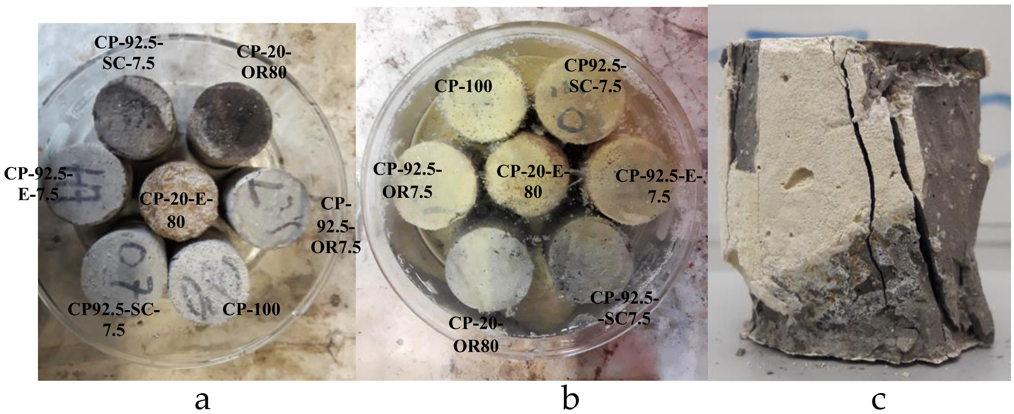

Figure 4. Specimens (**a**) before, (**b**) after acid attack, and (**c**) CP-20-OR-80 after acid attack and compressive strength testing.

3.3. Leaching Results

The construction materials must not pose a hazard to the safety, health, or hygiene, of occupants, neighbors, or workers. Moreover, they must not have a high impact on the environment during their useful life. Although, there are no specific regulations on the emissions of heavy metals in hydraulic road binder-containing wastes in Europe. Italy [39] and Portugal [40] have national regulations and Spain presents some regional regulations (Catalonia [41] and Basque Country [42]) for the recycling of the wastes in construction materials according to the European standard leaching test EN12457-4, the same one the European Union uses to limit the emissions of leaching heavy metals in waste landfills [38]. All use the same test but establish different limits for the same elements.

The European Directive defines three waste categories: hazardous, non-hazardous, and inert wastes. Table 4 compares leaching data from the three wastes and Portland cement to the European Directive limits [38]. Regarding [38], OR can be considered a non-hazardous waste due to its As and Pb content being higher than the inert limit and lower than the non-hazardous limit. Scallop and eggshells can be considered inert wastes. In Portugal, waste recycling is allowed by the Portuguese Environment Agency [39] when limits for the inert waste of [38] are not exceeded in construction materials. Both shells could be reused, but not biomass fly ash.

On the other hand, Italian Ministerial Decree 5 [40] establishes the maximum limits that waste must leach if it wants to be used in construction according to EN12457-4. Regarding the Italian Decree [40], Table 4 shows that OR (and CP) cannot be used in construction materials in Italy due to high values of Se, Pb, Ni, Mo, Cu, and As. Scallop and eggshells meet all the requirements in Italian legislation.

In Spain, there are no established national limits about the leaching emissions of hazardous heavy metals of construction materials containing wastes. However, for example in the case of Spain, there are regional laws that allow, based on the results of EN 12457-4, the establishment of whether waste can be used in specific construction applications (pavements, roads), such as the Autonomous Government of Catalonia and Basque Country. These legislations establish different limits for the same compounds (and are different from the Italian and Portuguese norms). They even establish limits for compounds that are not limited in others (i.e., Hg, Pb, Sb, As, and Cu are limited in Catalonia and not in Basque Country and, V is limited in Basque Country and not in Catalonia). These limits can be observed in previous studies [58]. According to these limits. scallop and eggshells can be used but biomass fly ash exceeds the limits regarding Se, Mo, and Ni in both regulations and Pb, As, and Cu in Catalonia limits.

Table 4. Results of EN 12457-4 leachability test and limits stated in the European landfill directive and Italian regulations.

Leaching Limit (mg/kg, Dry Base)					Leaching Results (mg/k, Dry Base)			
1999/31/Ec [41]								
Element	Hazard	Non-hazardous	Inert and Portuguese limit [42]	Italian limits [43]	Cement	Scallop shell	Eggshell	Biomass fly ash
Zn	200	50	4	0.03	1.1	≤0.03	≤0.03	0.02
Se	7	0.5	0.1	0.1	≤0.1	≤0.1	≤0.1	0.4
Sb	5	0.7	0.06	-	≤0.1	≤0.1	≤0.1	0.2
Pb	50	10	0.5	0.5	≤0.1	≤0.1	≤0.1	9.2
Ni	40	10	0.4	0.1	≤0.1	≤0.1	≤0.1	1.2
Mo	30	10	0.5	-	≤0.1	0.2	0.7	1.7
Hg	2	0.2	0.01	0.01	≤0.1	<0.1	<0.1	<0.1
Cu	100	50	2	0.5	0.5	0.1	0.8	6.5
Cr (total)	70	10	0.5	0.5	0.6	<0.2	<0.2	<0.2
Cd	5	1	0.04	0.05	<0.03	<0.03	<0.03	<0.03
Ba	300	100	20	10	0.4	0.9	1.2	0.3
As	25	2	0.5	0.5	≤0.3	≤0.3	≤0.3	1.7

3.4. Radiological Results

Table 5 shows the activity concentration values of ^{232}Th, ^{226}Ra, and ^{40}K. All specimens showed activity concentrations for ^{226}Ra and ^{232}Th lower than typical concentrations for concrete in the EU [59] (35 Bq/kg for ^{232}Th and 60 Bq/kg for ^{226}Ra), but values above 392 Bq/kg for ^{40}K (EU average) were achieved. Binders containing other wastes (such as titanium dioxide waste [60] or red mud [61]) present higher activity concentrations than OR (of ^{226}Ra and ^{232}Th), sin embargo when co-combustion fly ash is used [62] the activity concentrations are lower than OR but higher than egg and scallop shells. In particular, the behavior of specimens composed of biomass fly ash is noteworthy (CP-20-OR-80 and CP-92.5-OR-7.5).

Table 5. Activity concentrations (Bq/kg) of ^{40}K, ^{226}Ra, and ^{232}Th. Note: CP: Portland cement; SC: scallop shells; E: eggshell; OR: biomass fly ash.

Specimens	^{40}K	^{226}Ra	^{232}Th
CP-100	192 ± 9	30.5 ± 1.3	23.9 ± 3.2
CP-20-E-80	46.4 ± 3	8.2 ± 0.5	5.3 ± 0.4
CP-20-SC-80	53.3 ± 5.6	7.5 ± 0.4	5.1 ± 0.5
CP-20-OR-80	3683 ± 154	18.8 ± 1.8	20.6 ± 1.5
CP-92.5-E-7.5	179 ± 9	27.6 ± 1.2	19.2 ± 1.2
CP-92.5-SC-7.5	176 ± 9	29.8 ± 1.2	20.4 ± 1.2
CP-92.5-OR-7.5	449 ± 19	27.6 ± 1.7	20.6 ± 1.7

The component responsible for this radioactivity concentration value, which is an order of magnitude higher than the average, must be the OR incorporated into the material. During the growing process, olive pomace is naturally enriched in potassium (radioactive and stable isotopes) from fertilizers and soil. When olive pomace is used as biofuel, it has a K_2O concentration of up to 22.5%, which corresponds to 5200 Bq/kg. When fly ash is added to a road-base binder in an 80%wt ratio, ^{40}K activity concentrations can be estimated to be around 4000 Bq/kg, which corresponds to the CP-20-OR-80 activity.

On the contrary, construction materials containing sea and eggshells did not have either ^{40}K or nuclides from the ^{238}U and ^{232}Th series. Their activity concentrations were the lowest values found in this study, even lower than road-base binders containing only Portland cement. The potassium concentration in the shells was very low (<0.2% in Table 1). The inclusion of these shells dilutes the concentration of natural activity of the cement itself by removing any additional activity.

As shown in Table 6, almost all specimens produced an I index lower than 0.5; those of cement and mixes of cement with seashells and eggshells are three times less than those of OR. This finding suggests the possibility of using these matrices as dilution agents for building materials. CP-92.5-OR-7.5 also produced a dose rate lower than 0.3 mSv/y. However, when the dosage of OR increases to 80% (CP-20-OR-80), the dose rate is higher than 0.3 mSv/y, and its use should be restricted, but it could be used for restricted uses (boards, tiles, etc.) or superficial materials.

Table 6. Activity concentration index (I), radium equivalent activity (Ra_{eq}), absorbed (D), and effective dose rate (E). Note: CP: Portland cement; M: scallop shells; E: eggshell; OR: biomass fly ash.

Specimens	I	Ra_{eq} (Bq/kg)	D (nGy/h by Bq/kg)	E (mSv/y)
CP-100	0.29 ± 0.02	79.5	36.5	0.179
CP-20-E-80	0.07 ± 0.01	19.4	8.9	0.044
CP-20-SC-80	0.07 ± 0.01	18.9	8.8	0.043
CP-20-OR-80	1.39 ± 0.06	331.8	174.7	0.857
CP-92.5-E-7.5	0.25 ± 0.03	68.8	31.8	0.156
CP-92.5-SC-7.5	0.26 ± 0.03	72.5	33.4	0.164
CP-92.5-OR-7.5	0.34 ± 0.04	91.6	43.9	0.215

Regarding the Ra_{eq} of the materials, it can be noticed that no specimens show Ra_{eq} higher than 370 Bq/kg (the recommended value). The lowest values were obtained for CP-20-E-80, CP-20-SC-80, CP-92.7-E-7.5, and CP-92.7-SC-7.5.

Finally, except for CP-20-OR-80, most samples forecasted absorbed dose rates and annual effective doses were lower than the global average indoor absorbed dose rate (84 nGy/h) reported in UNSCEAR Annex B [49]. CP-20-OR-80 had values above the limit and should be ruled out for use in building materials. All maximum annual effective doses are below 1mSv/y [48].

3.5. Statistical Results

Pearson's correlation coefficients (r) were calculated and are shown in Figure 5. A positive correlation was observed between thorium and radium with correlation coefficients of r = 0.933, but not with ^{40}K. The role of potassium is completely independent of the other natural radioactive chains in the samples analyzed. ^{226}Ra and ^{232}Th showed a positively significant correlation with Mn, Ti, and S, while they showed a negative correlation with organic C at the significance level of r = −0.892 and r = −0.988, respectively. ^{40}K exhibited a positive correlation with Si, Al, Na, P, and Mn (and, of course, with oxide K_2O), suggesting that they have a common origin. Furthermore, a negative correlation was observed between the radionuclide ^{40}K and Ca (r = −0.962). Since this element is highly abundant in seashells and eggshells, it confirms that materials containing it will have a low radioactivity concentration of ^{40}K.

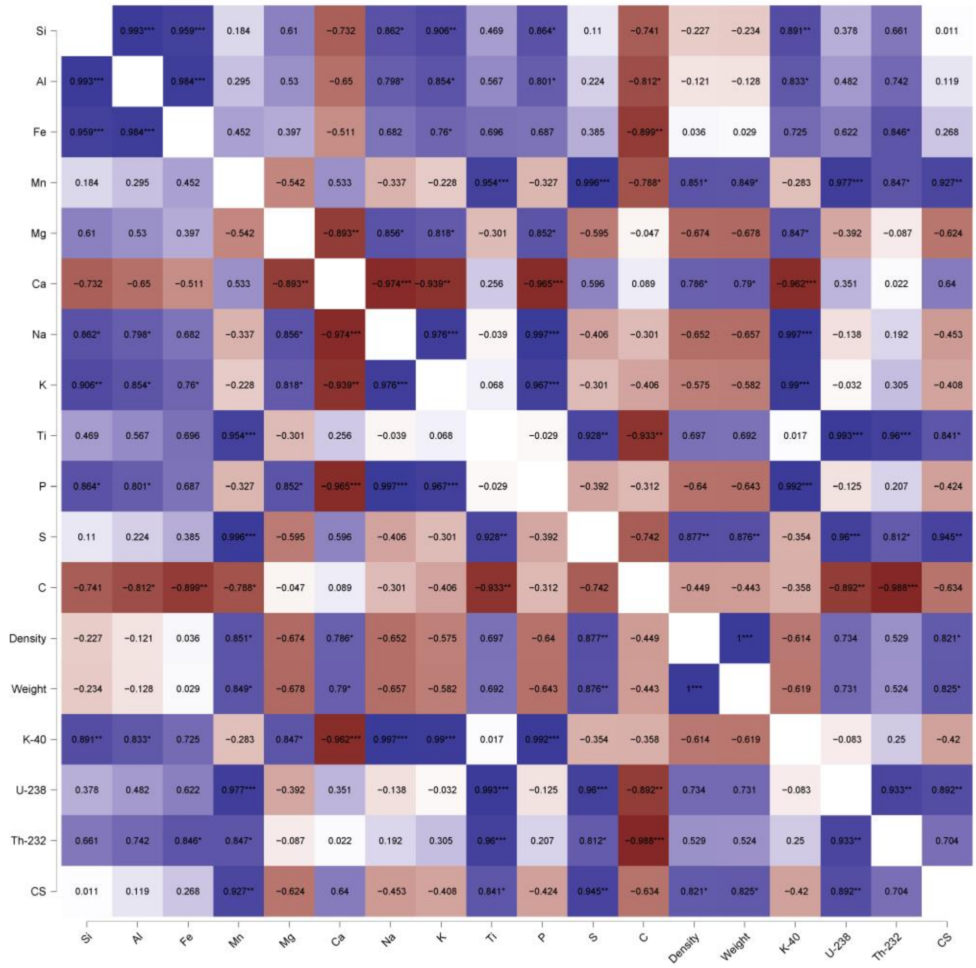

Figure 5. Heat map of Pearson's r correlation values of activity concentration and physicochemical com-position of building samples with significance level expressed by asterisks (*** p-value $\leq$ 0.001, ** p-value $\leq$ 0.05, * p-value $\leq$ 0.1).

Concentrations of elements were also tested for any correlation with the physicochemical properties of the materials. Most elements were significantly correlated with each other. Iron was significantly correlated with Si and Al (r = 0.959 and r = 0.984, respectively). From the results, it can be concluded that Ca concentration has a strong negative correlation with Mg, Na, K, and P content. In the case of CS, it had a strong positive correlation with Mn (r = 0.927) and S (r = 0.945). The CS content also showed a strong correlation with ^{238}U content.

4. Conclusions

The density and compressive strength of road-base binders decreased when different wastes were added in every proportion. Additions of 7.5% of both shells reduce the density to about 2.5% and the compressive strength to 20%, while 80% reduces the density to 20% and the compressive strength to 90%, while the addition of biomass fly ashes decreases the density and compressive strength in a higher proportion than shells. For all wastes, only a waste content of 7.5% satisfies the mechanical requirement for normal hardening road-base binders. Acid attack coefficients are increased when the three wastes are used, and this increase is greater when the waste dosage is increased (1500% more for biomass ash and 1000% higher for both shells)

With respect to leaching, scallop and eggshells can be considered inert wastes and can be used as a component of construction materials in accordance with Italian or Spanish regional limits. Fly ash from the combustion of olive pomace can be considered non-hazardous waste. It presents leaching values higher than Italian limits (Se, Pb, Ni, Mo, Cu, and As) and could not be used as a material in construction material according to all the different limits.

From a radiological perspective, all specimens showed activity concentrations for ^{226}Ra and ^{232}Th lower than the activity concentration for concrete. Only olive pomace ash showed higher values for ^{40}K than the EU average, producing road-base binders with an activity concentration index higher than 1. Therefore, its use would not be recommended. No specimens show Ra_{eq} higher than the recommended value.

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