Cleaner Design and Production of Lightweight Aggregates (LWAs) to Use in Agronomic Application

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Abstract: This research focused on the obtainment of sustainable lightweight aggregates (LWAs) for agronomic application. The cleaner production is based on saving matter through the valorization of waste available in industry as a substitute of clays into the formulation of the lightweight aggregates (LWAs). Three different types of clays (white, black, and red) and alternative raw materials were blended. Cattle bone flour ash (CBA) and a fertilizer glass (FG) were used to introduce K and P into the mixture in amounts suitable for fertilizer application, and a sewage sludge from a brewery wastewater treatment plant was used as pore forming agent. For the production of the LWAs, we mixed different percentage of waste in two different clay mixtures, which were thermally treated at 1000 °C for 1 h. Technological parameters such as loose bulk and oven dry density, total porosity, water absorption capacity, pH, and electrical conductivity were determined to evaluate the potential use of LWAs as a growing media. Moreover, scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) techniques were used, and leaching tests were performed to complete the samples’ characterization. The results indicated the potential for manufacturing high-quality LWAs for the agronomic field by using energy-saving and matter-processing involving low temperatures with respect to the conventional process.

Keywords: lightweight aggregates; agro-waste; growing substrate; fertilizers

1. Introduction

Ceramics materials are extensively studied as an alternative valorization of hazardous and non-hazardous waste and by-products for the production of sustainable construction materials to improve building energy savings [1] as an alternative to landfill disposal.

To deal with such problems, more attention has been paid to the development of sustainable clay bricks, such as those made from kindling from vine shoot [2], paper sludge [3], olive mill wastewater and spent coffee [4], grape and cherry seeds [5], sawdust and sugar cane ash [5], and textile laundry sludge [6]. Lightweight aggregates (LWAs) have also been extensively investigated through the addition of different organic and inorganic urban, industrial, and agro-waste, such as waste glass [7–10], bagasse, sludge and diatomaceous earth from the brewery industry [11], granite waste [12], fly ash [13,14], incinerator bottom ash [15,16], coal fly ash [17,18], waste engine [19–21], and sewage sludge [22–26]. The use of alternative energy sources for the production of lightweight aggregates has also begun to be studied. Franus et al. [27], in a recent research paper, used microwave radiation to produce lightweight aggregates from fly ash.
In terms of number of papers on this matter over past years, the publication rate has increased from 1 to 2 articles per year from the 1990s to 15–20 papers in recent years [28], demonstrating the great interest in this field; however, some topics are still open, such as the application lightweight aggregates (LWAs) in the agronomic field.

LWAs are characterized by a granular and porous structure with a loose bulk density no higher than 1.20 g/cm³ [29]. These characteristics are promoted by high-temperature heating treatment (1200–1400 °C), where clay pellets receive a thermal shock that causes the formation of a hard vitrified layer surface, preventing the run out of gases deriving from the combustion of different clay compounds. This behavior forces the material to swell. The vitreous phase plays a key role in bloating and in microstructural and physical properties of LWAs [25,28]. LWAs are generally composed of two types of materials that can produce glass phases and gases. To improve the inorganic oxide content in raw materials and control the viscosity of the glass phase, clay is still needed to produce satisfactory LWAs [25].

In this research, a sludge from a brewery wastewater treatment plant (BS) was incorporated as a pore forming agent in a clay formulation to reduce the sintering temperature using the exothermic reaction produced by the oxidation of organic matter within the clay matrix. The use of an energy-saving process (less than 200–300 °C) meant the possibility of obtaining materials with less environmental impact, boosting the local economy by offering innovative and sustainable materials.

LWAs are commonly used as hydroponic growth medium [30] or are mixed with other growth media such as soil and peat to improve drainage systems; moreover, they are also used as growing media/drainage layer for green roofing. The LWAs suitable for agricultural use would have specific physicochemical characteristics such as bulk density between 0.75 and 1.20 g/cm³, pH value in the range of 6.5–7.5, and electrical conductivity (EC) <2 mS/cm, as growing substrate conditions [31,32]. Therefore, this study was conducted to evaluate the feasibility of using different types of clays mixed with the above-mentioned BS as pore-forming agent, as well as cattle bone flour ash (CBA) and a fertilizer glass (FG) tailored by the authors bringing K and P to the mixture for the production of sustainable LWAs for sustainable construction. Moreover, we verified the chemical and physical properties of the materials, as the environmental characteristics have already been focused upon in a previous work [33], as well as the fertilizer capability of mixes containing ash or glass rich in P and K using mild conditions with respect to the current process.

2. Materials and Methods

2.1. Raw Materials Characterization

White (WC) and black (BC) clays were provided from a clay pit in Bailén, Jaén Province, Spain, and red clay (RC) came from a clay pit in Roncobotto, Modena province, Italy. The sludge from wastewater treatment plant (BS) was supplied by a brewery industry, Jaen province, Spain, and identified as non-hazardous waste (EWC 02-07-05). The cattle bone flour ash (CBA) and Glassy Sand (GS) were provided from local industries from Modena province, Italy. Calcined bone meal ash (CBA) was specially prepared for the experimental work by calcination of the flour (900 °C, 2h) and supplied by an Italian company that converts a wide range of meat industry by-products into protein flours for pet food. GS is a claimed glass derived from the secondary treatment, not classified as waste; it is a commercial product. Specific procedures are performed on the starting glass cullet to obtain shallow impurities (<0.068%), hence the fraction non-suitable for glassworks is submitted to a successive treatment to obtain two ends of waste: Glassy Sand (GS), with characteristics for glassworks, and ceramics sand, usually used in ceramic industry.

Raw materials were tested to determine their physical and chemical characteristics, as follows: total content of C, H, N, and S was determined by combustion in O₂ atmosphere using the CHNS-O Thermo Finnigan Elementary Analyzer Flash EA 1112. The
chemical composition was determined by X-ray fluorescence (XRF) using ARL-ADVANT’XP+ (THERMO equipment), Uniquant software. SiO₂, Al₂O₃ percentages, and the flux elements (flux = K₂O + Na₂O + CaO + MgO + FeO + Fe₂O₃) were recalculated from the original chemical composition and the loss on ignition (LOI) results, and these oxides were plotted on the Riley Diagram [34] on the theoretical suitability for bloating. The SiO₂/flux was also calculated for the same purpose, considering that a ratio >2 is typical for samples where suitable viscosity conditions are achieved [35,36].

X-ray diffractometry (XRD) was carried out using an automatic diffractometer PANalytical EMPIREAN, with radiation α1,2 (1.5406 Å) and slits (Soller) fixed at 1/4° and 0.04 rad. The measurements were performed from 5° to 80° 2θ for approximately 1 h with a step size of 0.0167°. The tube operated at 45 kV and 40 mA. The identification of crystalline phases was made by High Score Plus PANalytical software comparing with data on the JCPDS files. The samples were dried for 24 h at 105 °C and then pulverized in an agate mortar until the consistency of tcalc (<38.00 µm) was achieved.

A simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC-TG) was performed with a Mettler Toledo TGA/DSC 1 Thermal Analyzer equipment coupled with a Pfeiffer Vacuum ThermoStar TM GSD 320 mass spectrometer—approximately 10 mg of sample was tested in an Al₂O₃ crucible, O₂ atmosphere (80 ml/min), and a heating rate of 10 °C/min up to 1000–1200 °C.

2.2. Materials Preparation

Raw materials were dried in a stove at 105 °C for 24 h, after which they were pulverized with a ball mill until proper grain size (<0.10 mm).

The fertilizer glass (FG) was obtained by mixing the appropriates percentages of CBA, G5 as a parent glass, and potassium carbonate (K₂CO₃). The glass mixture was placed inside a refractory alumina silicate crucible for the melting treatment in an electric furnace (Lenton EHF 1700). The thermal cycle for glass fusion was 10 °C/min up to 800 °C and 20 min of isotherm, 10 °C/min up to 900 °C and 20 min of isotherm, 10 °C/min up to 1000 °C and 60 min of isotherm, 10 °C/min up to 1300 °C and 30 min of isotherm, 10 °C/min up to 1450 °C and 120 min of isotherm. To obtain a glass frit, we poured the molten glass mass into cold water, resulting in non-homogeneous grain size by the temperature contrast. The glass was ground up to 100 µm.

The fertilizer glass manufacturing leads to an increment of the costs and energy consumption during production. For that reason, aggregates formulated with FG were compared to samples made with CBA as an alternative raw material with low-energy consumption.

2.3. LWA Formulation

Two different clay-based mixtures were used for the production of LWAs: WBC (30% white clay–70% black clay) and RC (100% red clay). Table 1 shows the dosage of the different mixtures and the nomenclature adopted:

- Clays without waste (WBC and RC);
- Clays containing 15 wt % BS (WBBS15 and RCCBS15);
- Clays with 15 wt % of BS in addition to 10 wt % of glass (WBGC and RCGC);
- Clays with 15 wt % of BS in addition to 10 wt % of CBA (WBSCBA and RBCBA).

Table 1. The wt % components ratio in the studied aggregates.

| wt % | WC | BC | RC | BS | FG | CBA |
|------|----|----|----|----|----|-----|
| WBC  | 30 | 70 |    |    |    |     |
| WBBS15 | 25.5 | 59.5 | 15 |    |    |     |
| WBGC | 23 | 53.5 | 13.5 | 10 |    |     |
| WBCBA | 23 | 53.5 | 13.5 | 10 |    |     |
| RC  |    |    |    |    |    | 100 |
The raw materials were mixed in the established proportions with 10–12% water. Then, spherical balls with diameters between 11.96 and 21.68 mm were manually formed. Samples were dried at 105 °C for 24 h to reduce their moisture content and fired in an electric kiln (Lenton AWF13/12) directly at a sintering temperature of 1000 °C for 1 h to simulate thermal shock. The samples were left to cool by natural convection. As demonstrated in a preliminary study [37], the optimal amount of pore forming 15 wt % and the Tmax = 1000 °C for the thermal treatment were used in this research. Moreover, preparation of LWAS followed the handmade pelletization procedure set up previously.

### 2.4. LWAs Chemical–Physical Characterization

The physical properties of the sintered materials were determined as follows. The oven dry density (ρ_d) and water absorption (WA_d) were determined by the established procedure described by EN-ISO 1097-6 standard (annex C) [38]. The loose bulk density (ρ_s) and void percentage (Vr%) were determined according to EN-ISO 1097-3 standard [39].

pH (Digital pHmeter mod. PH6, XS/Eutech) and specific conductivity measures (E.C.) (Digital Conductimeter mod. COND6, XS/Eutech) were performed following the UNE-EN 13037 and UNE-EN 13038 standards [40,41].

The crushing strength of a single aggregate (S, in MPa) was determined in a series of 25 samples for each aggregate type so that each individual granule was crushed to failure using a Nannetti_FM 96 press, according to the following protocol: the distance between the aggregate loading points (D, in mm) was determined by measuring the diameter of the aggregate in the equilibrium position with a caliper. The pellet is then placed on the lower plate of the press, maintaining the initial position. The breaking load (Fc, in N) is recorded on the device. The value of S is determined by the following expression [42,43]:

\[
S = \frac{2.8 \times F_c}{\pi \times D^2}
\]  

The final result of S is the average of the 25 data obtained for each composition tested.

Microstructural analysis was performed using a scanning electron microscope SEM Quanta-200, coupled to a system for microanalysis X-EDS INCA-350 from Oxford Instruments. Samples were pasted it with epoxy resin on an aluminum sample holder and then metallized by sputter coating with a gold source (K550 Emitech).

Pore size distribution measurements were carried out by AutoPore IV Series (Intrusion Mercury Porosimeter) by Micromeritics (Norcross, GA, USA). Open porosity (Po) was evaluated using the time-set equilibrium (10 s) mode, pressure limits of 345 kPa and 228 MPa. This technique has already been used by numerous investigations to characterize the porosity of porous materials such as lightweight aggregates [44–46].

### 2.5. LWA Leaching Test

The leaching tests in water and citric acid medium were performed to evaluate the release capacity of nutrients (P and K) as well as of elements that for their quantity and type could be harmful for the environment. The tests were performed according to European regulations (Regulation EC 2003/2003 [47]; Legislative Decree 75/2010 [48]) in 2 different conditions: in water and citric acid (2% vol.) at 2 time intervals: 30 min to ensure the immediate release nutrients and 21 days to verify the slow release. The aggregates were tested in bulk and as powdered samples (<100 μm) in order to simulate the conditions in the soil. The samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS Agilent 7500a, Santa Clara, CA 95051, USA).
3. Results and Discussion

3.1. Materials Characterization

Elemental analysis (CNH-S) results of the three different types of clays are reported in Table 2. RC showed an almost complete absence of carbon while BC and WC contained low carbon content. Only black clay presented traces of sulfur. On the other hand, the wastewater sludge had a high carbon content, in line with other wastes of this type, and traces of S below those reported by other authors [49,50]; thus, the combustion process of BS will not generate SO₂ formation, which is an environmental benefit.

Table 2. Elementary CNH-S analysis of clay materials and wastewater sludge.

|       | % N  | % C   | % H   | % S  |
|-------|------|-------|-------|------|
| WC    | 0.04 | 4.35  | 0.45  | -    |
| BC    | 0.05 | 3.33  | 0.35  | 0.73 |
| RC    | -    | 0.92  | 0.69  | -    |
| BS    | 3.02 | 23.45 | 3.32  | 0.09 |

The chemical analysis (XRF) results reported in Table 3 show that white, black, and red clays contained high silica (SiO₂) and alumina (Al₂O₃) quantities, typical for these minerals, as well as iron oxide (Fe₂O₃), with red clay being the one with the highest values of the three oxides mentioned. A high amount of calcium oxide (CaO) in WC and BC in comparison to RC was observed, being attributable to the presence of carbonates, with white clay being the one with the highest percentages (20%). BS and CBA showed high amounts of calcium oxide (CaO), 18.52% and 53.89%, respectively. Regarding the other raw materials, we found that BS showed a high LOI (53.80%), probably due to organic matter content and carbonates (18.52% de CaO), making it suitable as a poring agent, while CBA and FG had high P and K content, respectively, confirming their use as a nutrient source. The results of the XRF analysis showed the absence of toxic substances for possible agricultural use.
Table 3. Chemical composition ($\sum_{\text{Flux}} = \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3$) and loss on ignition.

| OXIDE (%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3^a$ | MgO$^a$ | CaO$^a$ | Na$_2$O$^a$ | K$_2$O$^a$ | TiO$_2$ | P$_2$O$_5$ | SiO$_2$/∑FLUX | LOI |
|-----------|---------|-------------|---------------|---------|---------|-------------|----------|---------|-----------|---------------|-----|
| WC        | 43.9    | 8.5         | 3.3           | 2.1     | 20.0    | 0.2         | 1.6      | 0.4     | 0.1       | 1.6           | 19.9|
| BC        | 47.9    | 11.7        | 4.1           | 1.9     | 15.6    | 0.3         | 2.3      | 0.7     | 0.2       | 2.0           | 13.2|
| WBC       | 46.7    | 10.7        | 3.9           | 2.0     | 16.9    | 0.3         | 2.1      | 0.6     | 0.2       | 1.9           | --  |
| RC        | 52.8    | 17.9        | 7.9           | 3.9     | 2.6     | 0.7         | 2.9      | 0.8     | --        | 2.9           | 9.9 |
| BS        | 11.9    | 1.1         | 7.4           | 1.2     | 18.5    | 1.8         | 0.3      | 0.2     | 0.2       | 0.4           | 53.8|
| CBA       | 0.4     | --          | --            | 1.1     | 53.9    | 1.4         | --       | --      | --        | 41.2          | --  |
| GS        | 71.3    | 2.0         | 0.4           | 2.2     | 10.0    | 12.7        | 0.9      | 0.1     | --        | 2.7           | 0.2 |
| K$_2$CO$_3$ | --     | --          | --            | 0.1     | 0.5     | 74.2        | --       | --      | --        | 25.3          |     |
| FG        | 31.1    | 2.5         | 0.2           | 1.4     | 28.0    | 6.2         | 12.0     | --      | 18.5      | 0.7           | --  |

*Fluxing oxides.
As far as the mineralogical composition of the clays is concerned, it is worth highlighting the enormous similarity between Spanish clays due to their common origin. They presented the same majority, minority, and trace phases, with the exception of the illite, which is the minority phase of the WC, with plagioclase being present in the case of the WC (Table 4). The different origin of RC, comprising one-third of the clays in this study, was evident in the majority phases present in this clay, illite and kaolinite. It should also be pointed out that this clay had chlorite as a minority phase.

**Table 4. Mineralogy composition of the clays under study.**

| Clays  | Major     | Minor   | Traces |
|--------|-----------|---------|--------|
| WC     | Cal, Sm   | Q, Dol, Ill | Kao    |
| BC     | Cal, Sm   | Q, Dol, Pg | Kao    |
| RC     | Ill, Kao  | Q, Dol, Ch | --     |

Q = quartz; Cal = calcite; Dol = dolomite; Pg = plagioclase; Sm = smectite; Ill = illite; Kao = kaolinite; Ch = chlorite.

The thermal behavior of the LWA raw materials (clays and BS) was analyzed by DSC-TG [37]. As can be seen in Figure 1, at up to 600 °C, no significant differences were observed between the clays studied in terms of weight loss. Up to this temperature, in all cases, there was a loss of mass of approximately 3–6% due to the following processes in ascending order of temperature:

- hygroscopic water loss (up to 150 °C);
- interlayer water loss in illite and smectite (100–200 °C);
- organic matter decomposition (between 200–550 °C);
- dihydroxylation of illite (400–550 °C; [51]), kaolinite (530–590 °C), and/or chlorite (470–650 °C) [52];
- around 800 °C, endothermic event, decomposition of carbonates;
- between 900 and 1000 °C, exothermic event, peaks associated with the formation of calcium silicates;
- around 1200 °C, endothermic event corresponding to melting.

The endothermic processes are related to the typical loss of weight percentages according to the loss of moisture, dihydroxylation, and carbonate decomposition.

**Figure 1.** Differential scanning calorimetry and thermogravimetric analysis (DSC-TG) graphs of the clays (white clay (WC), black clay (BC), and red clay (RC)) and wastewater sludge (BS).
DSC-TG measurements in terms of BS showed that at up to 200 °C, there was a weight loss by the endothermic process due to the loss of moisture inherent in the material. In the range 200–600 °C, there were different exothermic peaks attributable to the combustion of organic matter, and we were able to distinguish between a first peak between 200 and 450 °C associated with the combustion of biodegradable materials, undigested organic material, dead bacteria, and semi-volatile compounds, and a second peak between 450 and 550 °C associated with the digestion of other materials. At around 700 °C, there was a small endothermic peak related to the decomposition of the carbonates present in the sludge (Table 3). From this temperature, the weight loss was stabilized. The total weight loss amounted to about 55% [49,53,54].

3.2. Sintered Materials

3.2.1. Chemical and Physical Properties

According to Fakhfakh et al. [36], if the SiO2/∑Flux ratio ≥ 2, the chemical composition of the sample is suitable to produce expansion when subjected to sudden heating at a high temperature. In Table 3, it can be seen how the RC met this condition, as well as the BC. However, the Spanish mixture of clay using WBC no longer complied with this condition as it had a value in the parameter of 1.9, slightly lower than 2.

Riley [34] and Ehlers [55] indicate in their works that lightweight aggregate is formed due to the development of a very viscous phase that is capable of trapping the gases released by the thermal alteration/decomposition of some mineral and/or organic species. Therefore, on the basis of the investigations of Riley [34] and Conley [56], we were able to determine a zone of chemical composition in a triangular diagram, which responded to the conditions of viscosity and bloating, i.e., to the conditions of expansion. In accordance with this, the sample located outside this region would in principle not be suitable for expansion. On the other hand, it is likely that mixtures located inside and therefore having the right chemical composition to form the necessary viscosity will not expand because the viscosity developed after the gases escaped to the outside. Therefore, Figure 2 shows how the RC clay and the RCB18 sample were located within the expansion area, while the rest remained outside it. Some of them, such as the RCB and the RCCBA, were very close to the limits of the area.
Figure 2. Representation of the aggregates studied in the Riley diagram [20].

Indicating the fact that the samples did not meet the Riley and Conley criteria or the SiO2/∑Flux condition is not a decisive process. Recent work indicates that these criteria are not totally reliable, and in many cases, it has been proven that lightweight aggregates are obtained from samples with compositions located outside the expansion zone [57,58].

The European standard EN-13055-1 [29] states that an aggregate is considered light if its ρ_b is <1.20 g/cm³ or its ρ_d is <2.00 g/cm³. On this basis, only the WBFG and WBCBA aggregates complied with the standard (Table 5), and therefore the rest of the mixtures tested would not be suitable to obtain lightweight aggregates according to the protocol established in the present investigation. However, although the WBBS15 sample did not comply with the limit requirement for ρ_b and the RCCBA and RCFG with that of ρ_d, the fact that their densities were very close to the established values allows these materials to continue to be considered interesting. The WBC, RC, and RCBS15 samples would not be suitable for the manufacture of lightweight aggregates under the conditions established in the study.

Table 5. LWA total intrusion volume (TIV) and total pore area (TPA) by mercury intrusion porosimetry (MIP).

| Parameters | WBC  | WBBS15 | WBFG | WBCBA | RC   | RCBS15 | RCFG  | RCCBA |
|------------|------|--------|------|-------|------|--------|-------|-------|
| Po (%)     | 47.60| 54.78  | 49.00| 51.73 | 22.16| 39.19  | 30.75 | 36.41 |
| TIV (cm³/g)| 0.33 | 0.44   | 0.38 | 0.40  | 0.11 | 0.23   | 0.18  | 0.21  |
| TPA (m²/g) | 1.20 | 1.37   | 1.13 | 1.40  | 1.82 | 1.39   | 1.20  | 1.41  |
Dondi et al. [28], after examining the results published by different authors, proposed a standard classification of light aggregates on the basis of their $\rho_b$. Using this classification, it can be established that WBCBA, RC, and RCBSBA aggregates showed a low density, while RCBSG, RCBSIS, WBC, WBBSIS, and WBC were classified in the medium density group. According to Dondi et al., low-density lightweight aggregates are the most common, representing about 40% of the aggregates considered in their study.

On the other hand, low-density values are related to high open porosity values (Table 6). As can be seen, the aggregates based on Italian red clay (RC) presented moderate porosities, which varied in the interval of 22.16–39.19%. These values were related to the WA$_{24}$ values presented by these aggregates (Table 5), which ranged from 7.27% for RC to 19.46% for RCCBA. When analyzing this series, we were able to see how the addition of the pore-forming agent (BS) to the initial clay produced an increase in the porosity of the aggregate obtained (RCBSIS) that was associated with an increase of WA$_{24}$ (19.01%). However, the addition of 10% FG or CBA glass caused a slight decrease in the associated porosity values, which were in accordance with the WA$_{24}$ values obtained. The decrease observed in the aggregate porosity may have been due to the glass phase provided by the FG or CBA, although the internal structure of open interconnected porosity was maintained.

Table 6. Technological properties of the aggregates: $\rho_b =$ loose bulk density; $\rho_d =$ oven dry density; WA$_{24}$ = water absorption after 24 h immersion; $V_v =$ void percentage; S = single aggregate crushing strength.

| Aggregate Name | $\rho_b$, g/cm$^3$ | $\rho_d$, g/cm$^3$ | WA$_{24}$, % | $V_v$, % | S, MPa | S$/\rho_d$, N/m$^2$ |
|----------------|-------------------|-------------------|--------------|---------|--------|-----------------|
| WBC            | 1.34              | 1.92              | 29.26        | 30.2    | 2.6    | 1.4             |
| WBBSIS         | 1.25              | 1.83              | 40.29        | 31.7    | 1.0    | 0.5             |
| WBFG           | 1.15              | 1.86              | 38.11        | 38.2    | 1.3    | 0.7             |
| WCBBA          | 0.72              | 1.80              | 39.86        | 60.0    | 0.8    | 0.4             |
| RC             | 0.81              | 2.32              | 7.27         | 65.1    | 9.6    | 4.1             |
| RCBSIS         | 1.34              | 2.19              | 19.01        | 38.8    | 6.2    | 2.8             |
| RCFG           | 1.19              | 2.14              | 16.99        | 44.4    | 5.7    | 2.7             |
| RCCBA          | 0.75              | 2.08              | 19.46        | 63.9    | 5.4    | 2.6             |

In the case of the series of aggregates obtained from the Spanish clay mixture (WBC), although the values of Po and WA$_{24}$ were higher ($\rho_b = 47.60–54.78%$; WA$_{24} = 29.20–40.29%$), the trend commented on in the previous series was maintained by the addition of glass or ashes.

Finally, the high water absorption values that they presented together with the fact that the WBCG and WBCBA specimens complied with the limits established by the standard to be considered as light aggregates made these materials very interesting to be used for agronomic purposes. According to the results of Table 6, the highest value of crushing strength was presented by RC (9.6 MPa), followed by the aggregates of the same series RCBSIS, RCFG, and RCCBA (5.4–6.2 MPa). This was directly related to its higher density and lower porosity. The rest of the aggregates presented low resistance values. In particular, the two materials mentioned above for their good aptitude for the use established in this investigation, WBCG and WBCBA, had values of 1.3 and 0.8 MPa, respectively, for this property, of the order of that declared for ARLITA Leca L (a commercial aggregate used in gardening, horticulture, and roof insulation applications). The technical guide ARLITA Leca [59] attributes a value of fragmentation and crushing strength of 0.7 MPa for this material.

Regarding pH values, the range presented by the soils was approximately 4 to 9, with the most normal values being between 5.5 and 8 and the most desirable levels in general falling in the neutral interval between 6.5 and 7.5 (neutral interval). Therefore, only the WCB aggregate was outside this range. On the other hand, all the aggregates manufactured presented values of E.C. <4 mS/cm, which can be classified as “slightly saline” if they were soils (Table 7) [60].
Table 7. Chemical properties of LWAs sintered at 1000 °C compared to WBC (30% white clay–70% black clay) and RC samples containing clays only.

| Parameters | WBC | WBBS15 | WBFG | WB_CBA | RC | RCCBS15 | RCFG | RC_CBA |
|------------|-----|--------|------|--------|----|---------|------|--------|
| pH         | 9.21| 7.42   | 6.98 | 8.00   | 7.16| 7.28    | 6.71 | 7.15   |
| EC (mS/cm) | 3.24| 1.74   | 1.12 | 1.98   | 1.15| 1.57    | 0.72 | 1.09   |

3.2.2. SEM Surface Analysis

Concerning the SEM analysis shown in Figure 3, the microstructure highlights two types of porosity that can be related to the clay material used. Samples made with red clay (RC) sintered almost completely at 1000 °C compared to the white–black mix of 30–70 wt% (WBC), confirming the differences in the water absorption values reported. From the SEM micrograph, we observed that the LWAs produced with WBC mix had more open porosity, and for this reason showed high water absorption percentage data. There was an increase of compactness related to the glass addition also in the less sintered samples constituted by WBC mixture. Otherwise, the addition of cattle bone flour ash (WBCBA and RCCBA) did not favor the sintering behavior, leading to less dense microstructure with respect to the glass addition. The cattle bone flour ash acted as an inert component into the mixture during the sintering process.

Figure 3. LWAs—SEM micrographs (600x) of (a) WBC, (b) RC, (c) WBBS15, (d) RCCBS15, (e) WBFG, (f) RCCFG, (g) WB_CBA, and (h) RC_CBA fired at 1000 °C.

3.2.3. Mercury Intrusion Porosimetry (MIP)

The pore volume distribution as a function of their diameter for the aggregates obtained is shown in Figures 4 and 5. The WBC aggregates obtained without the addition of waste were characterized by a multimodal pore diameter distribution with maxima between 1000 and 3000 nm. In contrary, RC-derived aggregates showed a monomodal pore diameter distribution with a maximum value at 438 nm. The addition of 15 wt% of BS generated greater porosity and a displacement of the size of the pore towards greater diameters [20,27]. It can be seen that the different pore diameters were in the interval of 100–30,000 nm for WBBS15 and 30–30,000 nm for RCCBS15. The addition of FG glass or CBA ash did not show any variation in the range of pore diameters with respect to aggregates obtained exclusively with BS.
According to those shown in Table 5 the values of open porosity (Po), total intrusion volume (TIV), and total pore area (TPA) of the manufactured aggregates. It can be seen how the volume of Hg introduced into the samples increased with the addition of BS, which once again highlights the pore-generating nature of the beer industry waste used. The trend observed in the TIV values was in accordance with the values obtained for the open porosity and WA24 of the aggregates.

Figure 6 shows the relationship between open porosity and water absorption for the two series of aggregates studied.
The behavior of both series was similar. The addition of BS produced a considerable increase in the open porosity in the aggregate associated with an increase in the water absorption value. Both parameters acquired the highest values for aggregates manufactured only with clay and this waste (WA24 = 40.29% and Po = 54.78% for the WCB series; WA24 = 19.01% and Po = 39.19% for the RC series). However, the vitrification capacity of the mixtures with FG generated the sealing of the superficial material layer, favoring the capacity of swelling, and creating larger pores and lower water absorption capacity [9]. As has been previously observed, the addition of FG caused the descent of porosity in almost 10.00%, which was also related to the water absorption capacity.

It can also be seen that the differences in the WA24 and Po values of the two clay-based mixtures, WBC and RC, were very substantial. The mineralogical composition of the clays (Table 4) showed that WC and BC had calcite (CaCO₃) as the majority phase and dolomite (CaMg(CO₃)₂) as the minority phase. These calcium and magnesium carbonates undergo a process of thermal decomposition. The temperature at which this phenomenon occurs depends on the chemical composition. Calcite decomposes at around 950 °C, while dolomite decomposes at around 850 °C, according to the following reactions:

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow \quad (2)
\]

\[
\text{MgCa}[\text{CO}_3]_2 \rightarrow \text{MgO} + \text{CaO} + 2\text{CO}_2 \uparrow \quad (3)
\]

The release of carbon dioxide during thermal decomposition reactions contributes to the appearance of porosity in these clays as the gases produced are trapped by the vitreous phase in formation. In addition, the formation of the vitreous phase is favored by the presence of the calcium and magnesium released, which can act as refractory elements, preventing the melting temperature from being reached and favoring the stabilization of the porosity before total melting is achieved. This would explain the high values of open porosity observed in the aggregates obtained from the WBC clay mix without additives (47.60%).

In contrast, the mineralogical composition of RC clay presents illite and kaolinite as its majority phases, minerals that present a high degree of vitrification. This, together with the absence of calcite and dolomite (the latter only appears as a minority phase), means that low porosity was generated in the aggregates obtained from RC (22.16%) [61,62]. This fact has been proven in previous studies [37].
3.2.4. LWA Leaching Test

The leaching test was performed following European regulation [47] in two different media, water (H₂O) and citric acid (C₆H₈O₇), in two time intervals in order to evaluate the released capacity of nutrients for samples with CBA (WBCBA and RCCBA) in comparison with samples with FG (WBF and RCF). Results are shown in Figure 7.

![Figure 7. LWA leaching test results (ppm) in water (H₂O) 30 min for whole samples (WS) and 30 min and 21 days in citric acid (C₆H₈O₇) for whole and powdered samples (PS).](image)

The release of bulk aggregates in a water medium is negligible compared to in citric acid at 30 min. The effect of grain size is essential for comparing the release data (ppm) obtained in citric acid in whole and powdered samples.

The test in citric after 30 min showed high release of phosphorus for all the bulk aggregates with FG, with regards to potassium with the mixtures WBFG and RCCBA, were the best.

At longer times (21 days), WBF released more amounts of P and K with respect to the RCF, and the WB mixtures sintered less with high open porosity (WA₂₄ = 38%), permitting exposure of a larger exchange surface to the acid medium, with this influencing the release results. Indeed, WBFG released potassium in higher proportions in almost all tests with respect to RCF. These observations support the microstructure analysis that highlighted different sintering degree depending on the clay matrix.

In particular, WBF and RCF showed better phosphorus-controlled release capability in a 21-days period. This fact confirms the positive effect of the presence of glass within the aggregates. The samples obtained with RC clay mix, as observed in SEM analysis, presented a more compact structure that allows a slow release of elements. The presence of cattle bone ash in the mixture did not contribute to the sintering, but played the role of an inert material, resulting in aggregates being more porous in comparison to those containing glass.

4. Conclusions

In this research, lightweight aggregates were successfully manufactured from two different clay matrices using brewery wastewater sludge as a pore-forming agent, and fertilizer glass and cattle bone flour ash as a means to give the materials fertilizing properties, studying the physical and mechanical properties of the aggregates obtained. On the basis of the results of this study, the following specific conclusions can be drawn:

- MIP results showed how brewery sludge can be efficiently used as pore-forming agent for LWA manufacturing, representing savings in virgin raw materials and energy consumption, as well as an alternative to landfill disposal.
The addition of FG or CBA produced a slight decrease in the open porosity and water absorption of the materials with respect to aggregates obtained only from BS. However, the open and interconnected porosity structure of the aggregates remained practically intact, as shown in the SEM images and the pore size distribution curves obtained by MIP.

Although some other materials were close to the limits, only WC_{FG} and WC_{CBA} were light aggregates according to the standard UNE-EN-13055-1:2003. Furthermore, these products had high water absorption values and crushing strength of the same order as commercial products such as Arlita Leca L used in gardening, horticulture, and roof insulation applications. Furthermore, they presented adequate pH and E.C. values, indicating their potential use as growth substrates in agronomic applications.

The results of the leaching tests showed the importance of grain size in the release of nutrients. For longer times (21 days) comparing clay aggregates with the same clay but containing FG instead of CBA, the former had a better capacity in the release of nutrients, showing the positive effect of the presence of the fertilizer glass.

The results indicate that the different clay minerals and waste/by-products had the potential for manufacturing high-quality, lightweight aggregates for agronomic purposes using low sintering temperature with less environmental impact and higher economic savings.

The use of brewery wastewater sludge and cattle bone flour ash for the production of lightweight aggregates brought about many environmental and economic benefits. Among the most important were the reduction of waste and energy savings. In addition, it allowed materials to be obtained that met the requirements set by the regulations to be declared as lightweight aggregates with new fertilizing properties. This approach to waste recovery makes it possible to reduce the consumption of non-renewable raw materials and the space allocated to waste disposal. This strategy is aligned with the principles of Circular Economy and Sustainable Development Goals.

**Supplementary Materials:** The following are available online at www.mdpi.com/2076-3417/11/2/800/s1: Figure S1: title, Table S1: title, Video S1: title.

**Author Contributions:** Conceptualization, Carmen Martínez-García and M. Teresa Cotes-Palomino; methodology, M. Teresa Cotes-Palomino, Luisa Barbieri, Fernanda Andreola and Isabella Lancellotti; validation, M. Teresa Cotes-Palomino, Luisa Barbieri.; formal analysis, Carmen Martínez-García, M. Teresa Cotes-Palomino, Luisa Barbieri, Fernanda Andreola and Isabella Lancellotti; investigation, Carmen Martínez-García, M. Teresa Cotes-Palomino, Luisa Barbieri, Fernanda Andreola, Isabella Lancellotti and Romina Farias; data curation, M. Teresa Cotes-Palomino.; writing—original draft preparation, Carmen Martínez-García, M. Teresa Cotes-Palomino, Luisa Barbieri, Fernanda Andreola, Isabella Lancellotti and Romina Farias writing—review and editing, Carmen Martínez-García, M. Teresa Cotes-Palomino, Luisa Barbieri, Fernanda Andreola and Isabella Lancellotti.; supervision, Carmen Martínez-García and M. Teresa Cotes-Palomino.; project administration, Carmen Martínez-García.

**Funding:** This research was conducted as a part of the SmartMats Project (MAT2015-70034-R), “Smart materials for sustainable construction”, funded by the Spanish Ministry of Economy and Competitiveness and FEDER (MINECO-FEDER).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Acknowledgments:** The authors thank Escavazioni Industriali Baroni S.P.A. for collaborating with this research. R.D. Farias would like to express her gratitude to the University of Jaen and University of Modena and Reggio Emilia. The authors gratefully acknowledge this support. The authors also gratefully acknowledge the technical and human support provided by CICT of the University of Jaén and the University of Málaga (UJA, MINECO, Junta de Andalucía, FEDER).

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