Journal of Cleaner Production 474 (2024) 143422

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Use of the organic fraction from recycled alkaline batteries in the manufacture of LECAs: Experimental and Environmental Assessment

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ARTICLE INFO

Handling Editor: Fu Zhao

Keywords:
Valorisation
Lightweight expanded clay aggregate
LECA
Density
Compressive strength
Organic fraction
Alkaline spent batteries
Circular economy
Life Cycle Assessment (LCA)

ABSTRACT

The industrial alkaline battery recycling process produces an organic fraction (OF) consisting of waste paper, plastic and cardboard. Currently, this OF is used for energy recovery, given the absence of a successful alternative recycling approach, attributed to its contamination and limited economic value. This study explored the valorisation of the organic fraction derived from the recycling of alkaline batteries as a foaming agent in the production of lightweight expanded clay aggregates (LECAs). The OF, was mixed with red stoneware atomized paste (RSAP) in varying proportions (5–30 wt%) and fired at temperatures between 1000 and 1200 °C. The volumetric expansion, density, and compressive strength of the resulting aggregates were determined via mineralogical and microstructural characterization. The results indicate the organic fraction's suitability as an expansion agent, particularly at 1200 °C with 5–15 wt% inclusion, showcasing density (0.65–0.75 g/cm^3) and compressive strength (1.34–1.39 MPa) comparable to commercial expanded clays. The microstructural analysis revealed the formation of rounded pores, influenced by the firing temperature and OF content. A Life Cycle Assessment (LCA) compared the environmental impacts of this process with traditional LECA manufacturing, highlighting the potential environmental benefits of using recycled battery waste. This study marks the first incorporation of this battery waste residue into LECA manufacturing, providing valuable insights into its environmental implications and paving the way for sustainable waste management practices.

1. Introduction

Lightweight aggregates are materials with a density not exceeding 2000 kg/m^3 or with a bulk density no greater than 1200 kg/m^3 (EN 130055-1, 2002). Most lightweight aggregates are produced from materials such as clay, shale, or slate (Ardakani and Yazdani, 2014; Anan and Abd El-Wahed, 2017; Ayati et al., 2018). Other materials, such as blast furnace slag, natural pumice, vermiculite, sepiolite, and perlite, can also be used as substitutes (Briao et al., 2020; Moreno-Maroto et al., 2021). Moreover, expanded clays are artificial lightweight aggregates characterized by a porous and uniform internal structure and a very resistant external layer (Rashad, 2018). Lightweight expanded clay aggregates (LECAs) are generally manufactured by mixing clay with other materials or compounds that have the capacity to generate gases, such as water vapour, CO_x, SO_x, O_2, F_2, and Cl_2, during thermal treatment. In the firing stage, gas generation and sintering of the outer layer must take place simultaneously so that the gases are trapped in the ceramic matrix; consequently, the expansion of the material occurs. In this way, light and economical materials with optimum technological properties are produced in terms of total density, porosity, mechanical resistance and water absorption capacity, which make them suitable for use as construction materials (Rashad, 2018).

LECAs are characterized by a low weight and a high surface area, which result in a great capacity for retaining water and the ability to immobilize organisms. For this reason, expanded clays have been used in different sectors, such as agriculture (Farias et al., 2017;

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https://doi.org/10.1016/j.jclepro.2024.143422
Received 3 January 2024; Received in revised form 28 May 2024; Accepted 15 August 2024

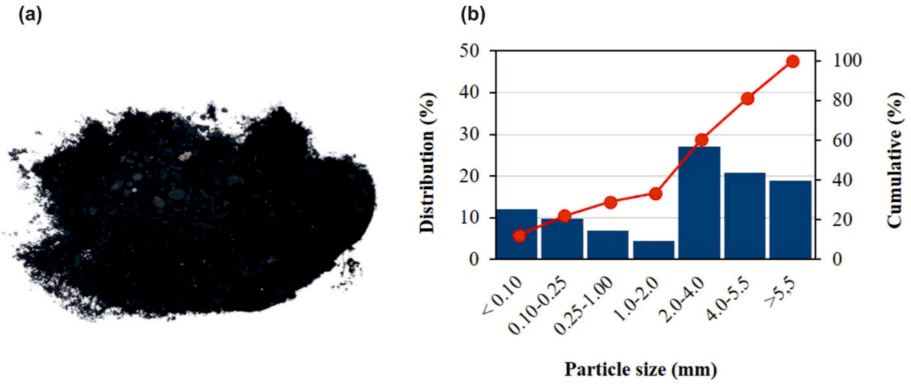

Fig. 1. a) Appearance of the as-received alkaline battery organic fraction waste (OF) and b) particle size distribution.

Martínez-García et al., 2021), sanitation (Moore et al., 1999) and construction (Rashad, 2018). In this last sector, LECAs have been employed for the manufacture of cement, structural clay, filler material, construction panels, ground adaptation materials, floating structures, acoustic and thermal insulation materials, etc. (Ardakani and Yazdani, 2014). Likewise, they have also been used in the manufacture of furnace linings, catalytic converters, membranes, adsorbents, biological filters and in water treatment (Pishdadi-Aghdarreh et al., 2023; Anan and Abd El-Wahed, 2017; Ayati et al., 2018; Briao et al., 2020).

Currently, environmental policies emphasize the need to increase the utilization rate of materials to preserve natural resources. This is the basis of the circular economy, which focuses on maximizing the use of available resources, i.e., lengthening their life cycle. Specifically, the aim of the circular economy is to reduce waste generation as much as possible but also to make the best use of waste that cannot be avoided. For this reason, in recent years, several studies have evaluated the possibility of total or partial replacement of natural raw materials by waste in the composition of lightweight aggregates. In this sense, mining waste clays (Bayoussef et al., 2021), coal combustion residues (Gonzalez-Corrochano et al., 2014), spent mineral adsorbents (Franus et al., 2011), sludges (Mahana et al., 2024; Martinez-Garcia et al., 2021; Franus et al., 2016a,b; Manosa et al., 2021; Cao et al., 2019; Korol et al., 2020), motor oil residues (Franus et al., 2016a,b; Burbano et al., 2021), automotive plastic waste (Liu et al., 2017), mining waste (Souza et al., 2021) and residues from different industries, such as glass (Jradi, L., Seif El Dine, 2023), wood (Bayoussef et al., 2021), food (Aguiar et al., 2024; Leal de Souza et al., 2021; Lyra et al., 2019; Martinez-Garcia et al., 2021; Menchavez and Intong, 2010; Moreno-Maroto et al., 2019; Souza et al., 2021) and paper (Dong et al., 2024), have been studied.

The construction industry demands a large amount of raw materials. In fact, the European Commission indicated that approximately 50% of all extracted raw materials are consumed by this sector (European Commission, 2021). However, this industry also has the capacity to absorb large quantities and different types of waste due to the diversity of the products it generates, the large amount of raw materials needed and the microstructural heterogeneity of construction materials.

In relation to the aggregates sector, the European Aggregates Association, in its last annual review, stated that the European demand for aggregates was more than 3000 million tonnes per year. Of these, 90.7% came from natural resources, and only 9.3% (279 million tonnes) corresponded to recycled and reused materials (Aggregates Europe Association, 2022). In view of this situation, it is necessary to increase the rate of use of recycled materials as replacements for natural resources.

On the other hand, in Europe, 229×10^3 tonnes of portable batteries were placed on the market, of which only 99×10^3 tonnes were recycled (Eurostat, 2023). In the battery sector, 2023 is key because the Battery Regulation has come into force to foster not only recycling but also the reintroduction of secondary raw materials in different types of industries (European Commission, 2023). In the recycling process of batteries, different types of waste are generated, including an organic fraction containing waste paper, plastic and cardboard. Considering that this organic fraction corresponds to approximately 10–20% of the initial weight of the battery, more than $8–16 \times 10^3$ tons of this waste were generated, supposing that 80% of the collected batteries were alkaline. The final end of this organic fraction is currently energy valorisation. To date, due to challenges in separating paper and plastic from the organic fraction contaminated by inorganic compounds from alkaline batteries, along with the low economic value of this waste fraction, no research or initiative has successfully identified an alternative solution to enhance recycling efficiency beyond energy valorisation.

Owing to its organic nature, this waste fraction could be considered an optimal raw material for the manufacture of lightweight aggregates since the release of gases that evolve during combustion could favour the expansion of clay. In addition, its heating value provides the system with part of the energy necessary for clay sintering. The incorporation of this waste would minimize the environmental impact associated with the overexploitation of natural resources in the manufacture of LECAs. Thus, the objective of this work was to study the use of the organic fraction of alkaline batteries as a foaming agent in the manufacturing of lightweight expanded clay aggregates. In this respect, different organic fraction/clay mixtures were pelleted and subjected to expansion trials at different temperatures. The volumetric expansion, density, and compressive strength of the expanded aggregates were determined, and their mineralogical and microstructural characteristics were studied. To provide a wider view of the use of battery-waste byproduct effects on materials, a Life Cycle Assessment (LCA) analysis of the LECA manufacturing process, including the organic fraction of alkaline batteries, was carried out. The process was compared to a conventional LECA fabrication process to assess and quantify the differences related to the environmental impacts of using this residue as a secondary raw material.

2. Materials and methods

2.1. Materials

As a base material for the manufacture of expanded clay, a red stoneware atomized paste (RSAP) was used. The waste used in this work as a blowing agent for the manufacture of LECAs was the organic fraction (OF) split during the alkaline battery grinding stage supplied by Envirobat España S.L. (Guadalajara, Spain). This solid waste is generated during the battery recycling process carried out in an industrial plant. The alkaline recycling process is a well-known mechanical size-reduction treatment. After a shredding process with blades, the product is divided into two main fractions: fine particles that are further separated into a magnetic and non-magnetic fraction; and on the other hand, a coarse fraction consisting of paper, plastic and other compounds, which is covered by the present study. Fig. 1 shows the

Table 1
Chemical composition (wt.%) of the red stoneware atomised paste (RSAP) and the organic fraction waste (OF) determined by X-ray fluorescence.

	CO_2	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O3	ZnO	ZrO_2	BaO	Sb_2O_3
RSAP	6.8	0.5	1.5	20.4	56.6	<0.1	<0.1	<0.1	4.2	1.8	0.9	<0.1	7.1	<0.1	<0.1	<0.1	–
OF	25.5	3.3	–	0.1	0.2	–	0.7	1.7	8.5	<0.1	<0.1	33.5	1.8	23.0	0.2	0.2	0.7

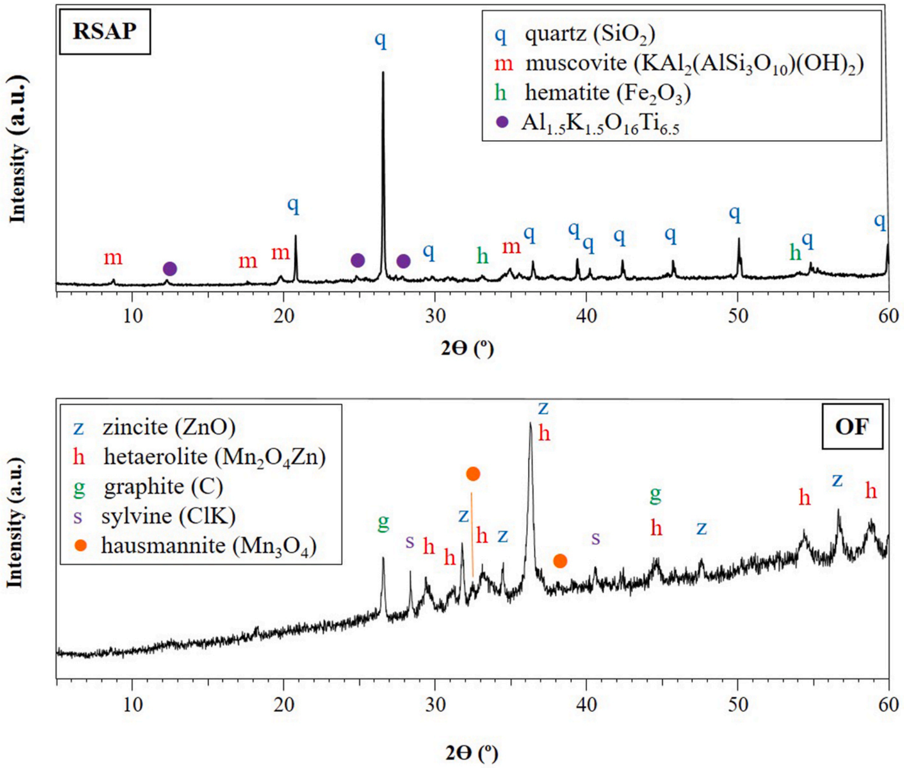

Fig. 2. XRD patterns of the red stoneware atomized paste (RSAP) and the organic fraction waste (OF).

appearance of the as-received sample and its particle size distribution. It consists of a granulated material that is black in colour and has a highly heterogeneous distribution of particle sizes, with an average size greater than 2 mm. A significant amount of fine dust, along with a fraction of larger particles of different shapes, colours and appearances, can be observed. This waste is considered non-hazardous according to the EWC code 19.12.12 (other wastes, including mixtures of materials, from mechanical treatment of waste, not containing dangerous substances) (Commission of the European Communities, 2010).

Table 1 shows the chemical composition determined by X-ray fluorescence (XRF), and Fig. 2 shows the X-ray diffraction patterns of RSAP and OF waste. RSAP is mainly composed of silicon, aluminium and iron oxides and is associated with the occurrence of muscovite ($KAl_2(AlSi_3O_{10})$ $(OH)_2$) and quartz (SiO_2), which are the main crystalline phases. Haematite (Fe_2O_3) is also detected as a minor phase. The organic waste fraction is a rather amorphous material that mainly comprises manganese and zinc oxides, such as zincite (ZnO) and hetaerolite ($ZnMn_2O_4$), as crystalline phases. Moreover, it also contains a significant amount of carbon associated with the presence of graphite. The chemical composition of RSAP is within the range of LECAS chemistry reported in the literature (Rashad, 2018). However, in a preliminary test it was found that RSAP exhibits no expansion ability during firing. In fact, the composition of RSAP, considering only silica, alumina and the total fluxing constituents ($(Na,K)_2O$, $(Ca,Mg)O$ and Fe_2O_3) lies outside the bloating clay composition area established by Riley (1951). This indicates that during heating, RSAP will not undergo natural expansion on its own. Any expansion observed will be due to the addition of the organic fraction waste. The bloating of clays during firing is closely related to their chemical composition. For bloating to occur, liquid phases must form in sufficient quantity and with appropriate viscosity to trap the gases released during firing. However, an appropriate chemical composition alone is not sufficient. The second condition necessary for bloating is the presence of certain minerals, or a combination of minerals, that dissociate and release gases once the clay mass has melted into a viscous state (Riley, 1951). While RASP contains a notable quantity of iron oxide, its contribution to expansion relies on its presence in the form of haematite (Fe_2O_3), which, during firing, undergoes transformation into wustite (FeO), thereby releasing O_2. Although haematite has been identified in the mineralogical analysis of RASP, the associated peaks exhibit low intensity, suggesting that the haematite content in RASP is likely insufficient to induce bloating.

2.2. *Manufacture of LECAs*

To use the as-received waste to prepare the expanded clay, preliminary tests were conducted following the procedure described below. The results showed that the compositions studied did not withstand the firing cycle, and the samples were completely disintegrated, probably due to the wide size heterogeneity of the organic fraction. Accordingly, the as-received sample was subjected to grinding and sieving steps to a size lower than 1 mm. Fine grinding was performed in a stainless-steel jar (250 mL) in a planetary mill (RETSCH PM 100) operating at a rate of 200 rpm, and high-grade steel balls (10 balls of 20 mm diameter) were used as grinding media.

Compositions incorporating different percentages of alkaline battery waste as a blowing agent in ceramic paste, ranging between 5 and 30 wt

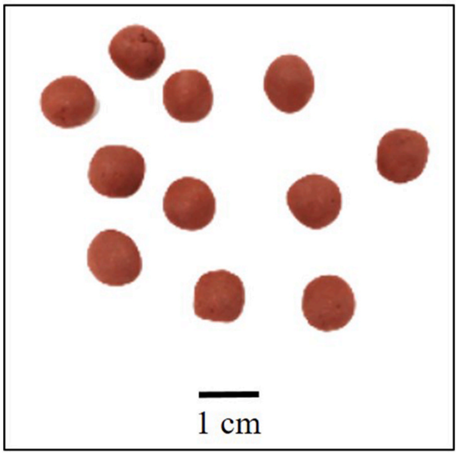

Fig. 3. Green pellets of a RSAP-5-OF sample shaped by manual blending.

%, were formulated. These compositions are denoted as RSAP-xOF, where x indicates the weight percentage of the organic fraction waste in the composition. The mixtures were homogenised for 15 min in a TURBULA mixer, operating at a speed of 50 rpm. Subsequently, 25 wt % water was added to the mixtures, and the pellets were manually moulded from 1.5 g of mixture, resulting in nearly spherical pellets with an average diameter of 10.5 mm. Fig. 3 presents a view of the as-prepared green pellets.

Firing experiments were performed at 1000, 1100 and 1200 °C using a Superkanthal electric kiln (Termiber). To this end, the green pellets were placed into the kiln previously heated to the fixed firing temperature and kept for 15 min. After the dwell time, the pellets were removed from the furnace and cooled in the air until they reached room temperature.

The procedure followed for the manufacture of LECAs in the laboratory is similar to other procedures reported in the literature (Bernhardt et al., 2013). However, in the present study, neither a drying stage nor a pre-treatment stage prior to the firing stage was included, which distinguishes it from other procedures described in the literature.

2.3. Characterization procedures

The volumetric expansion after firing was evaluated by estimating the volume (cm^3) of the expanded pellet by measuring its diameter (cm) with a calliper. To evaluate the expansion percentage, the pellets were considered to be spherical. For each pellet, ten diameter measurements were taken, and the mean diameter was calculated. The green pellet volume was 0.60 cm^3.

The bulk apparent density (g/cm^3) of the expanded clay aggregates was calculated from the measurements of their weight (g) and volume (cm^3). For each composition-temperature pair, the density was calculated as the average of the density of ten pellets.

Mineralogical analysis of the expanded clay was carried out by X-ray diffraction (XRD) using a Bruker DS Advance diffractometer with Cu K_α radiation working at 30 mA and 40 kV. The diffractograms were collected in the interval 5–60° (2θ), with a step size of 0.019736 and a time step of 0.5 s. XRD analyses were performed on expanded clay samples ground and sieved to a particle size less than 63 μm.

The compressive strength (MPa) of individual expanded clay aggregates was determined with a SERVOSIS 1000N testing machine. For the tests, the pellets were placed between the two plates, and the testing rate was adjusted to 0.2–0.3 mm/s so that failure would occur within 15–60 s. For each composition-temperature pair, the compressive strength was calculated as the average of ten pellets.

Microstructural examination of the expanded clay aggregates was performed via field emission scanning electron microscopy (FESEM) on a JEOL model JSM 6500F microscope with an accelerating voltage of 20 kV. SEM observations were performed on fresh fractured specimens covered with an Au-Pd layer in a Balzers SCD 050 sputter. Semi-quantitative analysis of the different phases was performed by energy dispersive X-ray spectroscopy (EDS) with a Link eXL detector provided by a beryllium (Be) window. The allocation of different elements was

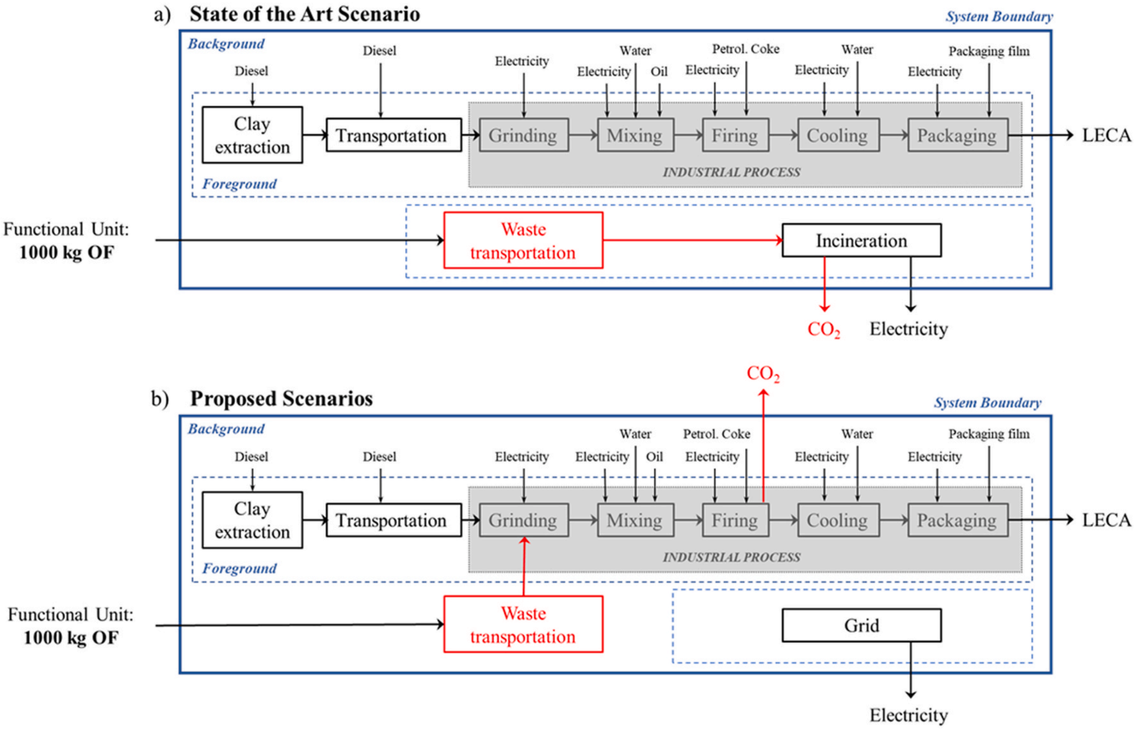

Fig. 4. LCA scenarios, a) State of the Art: LECA industrial manufacturing and waste valorisation, b) Proposed: inclusion of (waste) as secondary raw material in LECA manufacturing.

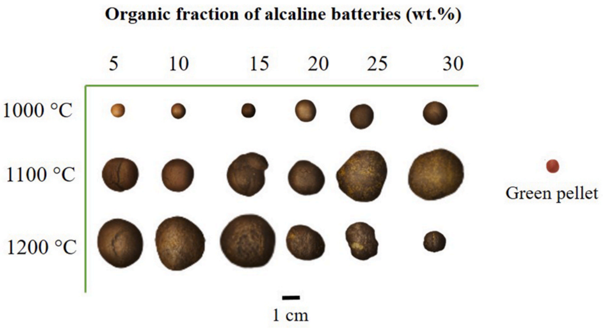

Fig. 5. Appearance of the pellets of different compositions after firing treatments at different temperatures (1000, 1100 and 1200 °C) for 15 min.

studied by using digital X-ray mapping.

2.4. *Life Cycle Assessment (LCA)*

Life Cycle Assessment (LCA) is a methodology used to evaluate the environmental impacts associated with all stages of the life cycle of a commercial product, process or service. An LCA study requires a detailed inventory of the energy and materials used in the entire product value chain, and estimates the emissions released. With these figures, the potential cumulative environmental impacts are determined. In this study, the LCA was calculated following the ISO 14040/14044 standards in four different steps: goal and scope of the study, life cycle inventory, impact assessment, and interpretation of the results.

2.4.1. *Goal and scope*

The goal of this analysis is to calculate the environmental impacts associated to the manufacture of LECA including OF from alkaline batteries recycling as blowing agent, and to compare them with similar processes using only natural raw materials. Since the waste (OF) incorporation does not influence the use and end-of-life phases of the LECA, a cradle-to-gate (from the extraction and processing of the raw material, *cradle*, to its manufacture, *gate*) approach were evaluated for several scenarios. The distribution, use of the product, and recycling or final disposal of the materials (*grave*) were therefore not included.

Fig. 4 represents the different analysis scenarios proposed, including the industrial manufacturing of LECAs from exclusively natural raw materials (Fig. 4a, adapted from Quina et al., 2020). The process comprises the extraction of clay and its transport to the industrial processing plant where LECAs are manufactured. The main stages of the industrial process are grinding, mixing, firing, cooling and packaging. The system boundaries also include the current process of management, namely, energy recovery to obtain electricity. By introducing OF into the manufacture of LECAs, this energy would no longer be generated. Consequently, to balance the whole system, the electricity that is not produced was assumed to be supplied by the grid. In the manufacturing of LECAs, OF could be directly added at the grinding stage (Fig. 4b), and as OF replaces different percentages of natural clay, no deviations in resource consumption were assumed. The CO_2 emissions from waste are allocated to the firing step.

2.4.2. *Inventory analysis*

The inventory analysis was based on data from the literature (Quina et al., 2020), where an industrial LECA manufacturing process using natural clay was evaluated. However, as this study requires additional experimental data related to the residue lower heating value, waste transport and CO_2 retained in the final product, further relevant data will be addressed in the Results and Discussion section.

The software used was *SimaPro v.9.5*, with *Ecoinvent v.3.9* database and the method employed, *Environmental Footprint 3.1 (adapted)*.

Table 2
Average volumetric expansion (%) experimented by the pellets during the firing process.

Composition	1000 °C	1100 °C	1200 °C
RSAP-5-OF	2.5 ± 0.2	44 ± 3	96 ± 5
RSAP-10-OF	2.9 ± 0.2	33 ± 2	116 ± 6
RSAP-15-OF	1.7 ± 0.1	78 ± 5	128 ± 6
RSAP-20-OF	6.7 ± 0.5	51 ± 4	61 ± 5
RSAP-25-OF	14.8 ± 0.9	106 ± 4	38 ± 3
RSAP-30-OF	11.4 ± 0.9	125 ± 5	10.0 ± 0.8

3. Results and Discussion

The appearance of the pellets of different compositions obtained after expansion treatments at varying firing temperatures for 15 min is shown in Fig. 5, along with a green pellet for comparison. At first glance, the marked effects produced by the different experimental conditions studied, i.e., temperature and percentage of added residue, on the expansion of clay aggregates were observed. The volume expansion is highly significant for working temperatures of 1100° and 1200 °C. It is also observed that the expansion rate increases as the waste percentage increases for tests performed at 1100 °C but decreases at a firing temperature of 1200 °C.

The values of the volumetric expansion of the pellets during the firing process, determined by comparing the fired aggregates with the green sample, are shown in Table 2.

After heat treatment at 1000 °C, the volumetric expansion of the pellets was restricted, and to the visual inspection, the volume of the fired pellets did not change significantly. During firing, the thermal expansion of clay is caused by the burning of organic matter and the release of gases (Moreno-Maroto et al., 2021). However, for bloating to occur during firing, two conditions must be met: (1) liquid phases must form to fill the pore spaces between the particles, thereby trapping the gases formed; and (2) the molten material must be sufficiently viscous to prevent the gas from escaping. At 1000 °C, the pellets do not undergo significant expansion, as shown by the low volumetric expansion values (<15% at 1000 °C) regardless of the percentage of introduced as an additive. This result indicates that either the RSAP mass has not melted, or if it has, the melt is not viscous enough to trap the gases released by the combustion of. From 1100 °C onwards, the feldspathic phase present in the clay begins to form liquid phases, decreasing the viscosity of the ceramic matrix (Rashad, 2018). Under these conditions, the gases generated by the combustion of organic waste can leave the ceramic matrix, leading to the expansion of the material. In general, at 1100 °C, expansion increases with the percentage of waste added to the composition. In materials fired at 1200 °C, the volumetric expansion initially increases with the OF content for samples prepared with a percentage of waste ≤15%; however, from a percentage of 15% onwards, the greater the incorporation of blowing agent is, the lower the volumetric expansion is, i.e., the expansion is inhibited as the waste percentage in the mixture increases. This result indicates that the organic fraction of alkaline batteries acts in two different ways, depending on temperature, during clay firing. On the one hand, the release of gases generated during combustion promotes the expansion of clay; on the other hand, the presence of metals or metal oxides favours the formation of liquid phases in the ceramic matrix, decreasing its viscosity and, therefore, the final expansion.

Fig. 6 shows the variations in the density and compressive strength of the expanded pellets with respect to the organic fraction percentage and firing temperature. The coloured area marks the density and strength range specified in the data sheets of different commercial expanded clay aggregates with similar granulometry. Density values in the range of those of commercial lightweight aggregates are achieved for samples fired at 1200 °C (5–15 wt% OF) and 1100 °C (25–30 wt% OF). Nevertheless, all the tested compositions resulted in aggregates with particle density values less than 2000 $kg/m^{3;}$ hence, all the aggregates may be

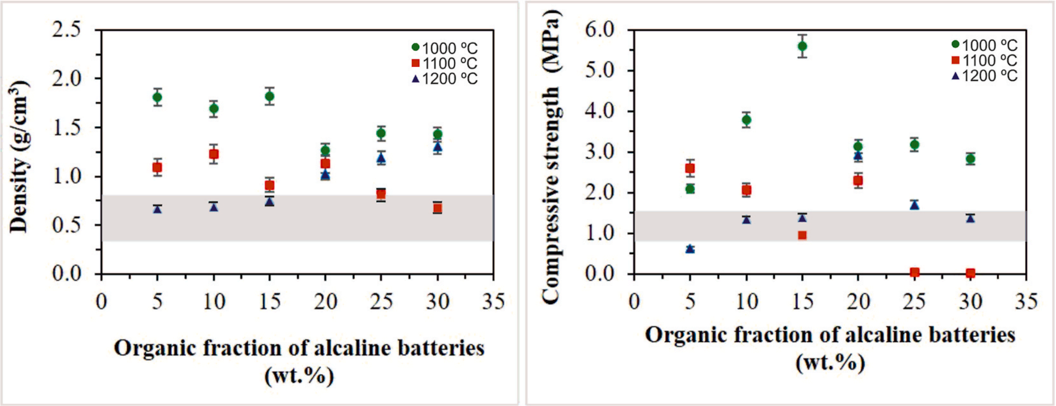

Fig. 6. Density (g/cm^3) and compressive strength (MPa) of the expanded aggregates obtained at different experimental conditions (percentage of organic fraction, 5–30 wt%, and firing temperature, 1000–1200 °C). The coloured area marks the density range of commercial expanded clay aggregates with similar granulometry.

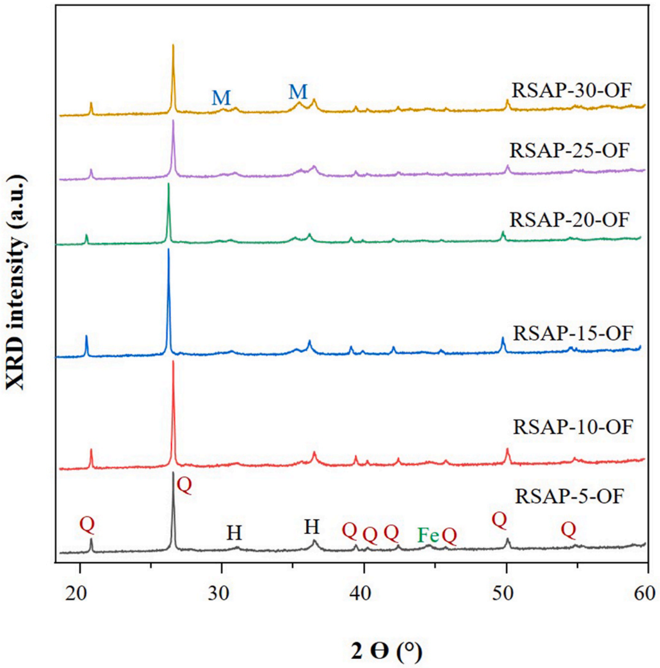

Fig. 7. X-ray diffractograms of pellets of different compositions fired at 1200 °C for 15 min (Q = quartz (SiO_2); H = hercynite (Al_2FeO_4); M = magnetite (Fe_3O_4); Fe = iron).

considered lightweight aggregates. Therefore, from the density and volumetric expansion results, it is deduced that the organic fraction of alkaline batteries could be a suitable material for producing expansion during the firing of clay bodies; thus, it can be used as a blowing agent in the manufacture of expanded clays. Concerning compressive strength, except for the case of materials fired at 1100 °C with 25–30 wt% of organic fraction, the rest of the formulations presented compressive strength values similar to or higher than those of commercial expanded clays. Furthermore, the compressive strength values are consistent with those reported in the literature. For example, the compressive strength ranges from 2.45 to 8.41 MPa in LECAs derived from bentonite-additivated clays (Abdelfattah et al., 2020) and has a mean value of 2.87 MPa in LECAs produced with waste engine oil as the blowing agent (Burbano et al., 2021). These values also align with the compressive strength values reported for ultra-lightweight ceramsite made from non-expanded clay and waste sawdust, which range from 1.0 to 3.5 MPa (Pei et al., 2021). Therefore, the joint analysis of the density and compressive strength results highlights that the RSAP-5-OF, RSAP-10-OF and RSAP-15-OF compositions fired at 1200 °C yield lightweight ceramic materials with density and compressive strength properties in the range of those of commercial expanded clays.

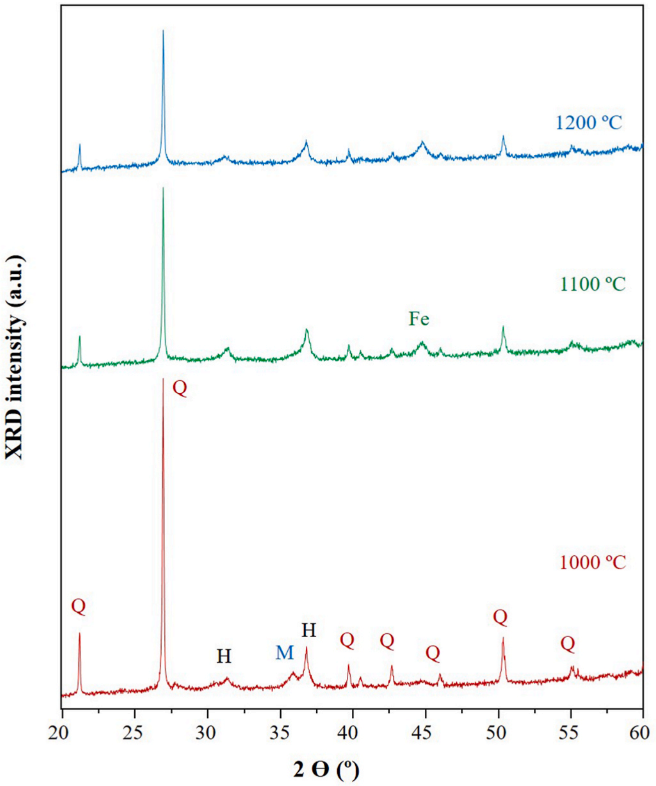

Fig. 8. X-ray diffractograms of pellets of RSAP-15-OF composition fired at different temperatures for 15 min (Q = quartz (SiO_2); H = hercynite (Al_2FeO_4); M = magnetite (Fe_3O_4)).

Fig. 7 shows the X-ray diffractograms of pellets of different compositions fired at 1200 °C. The XRD patterns are quite similar, revealing quartz (SiO_2) and hercynite, a spinel-group mineral with the formula Al_2FeO_4, as the main crystalline phases. As the percentage of residue incorporated in the ceramic paste increased, two peaks associated with the magnetite phase ($Fe_2O_3 \cdot FeO$) appeared and became more intense in the diffractograms of the fired samples. The formation of magnetite is probably associated with the partial reduction of Fe(III) from haematite to Fe(II), favoured by a reducing atmosphere as a result of CO and H_2

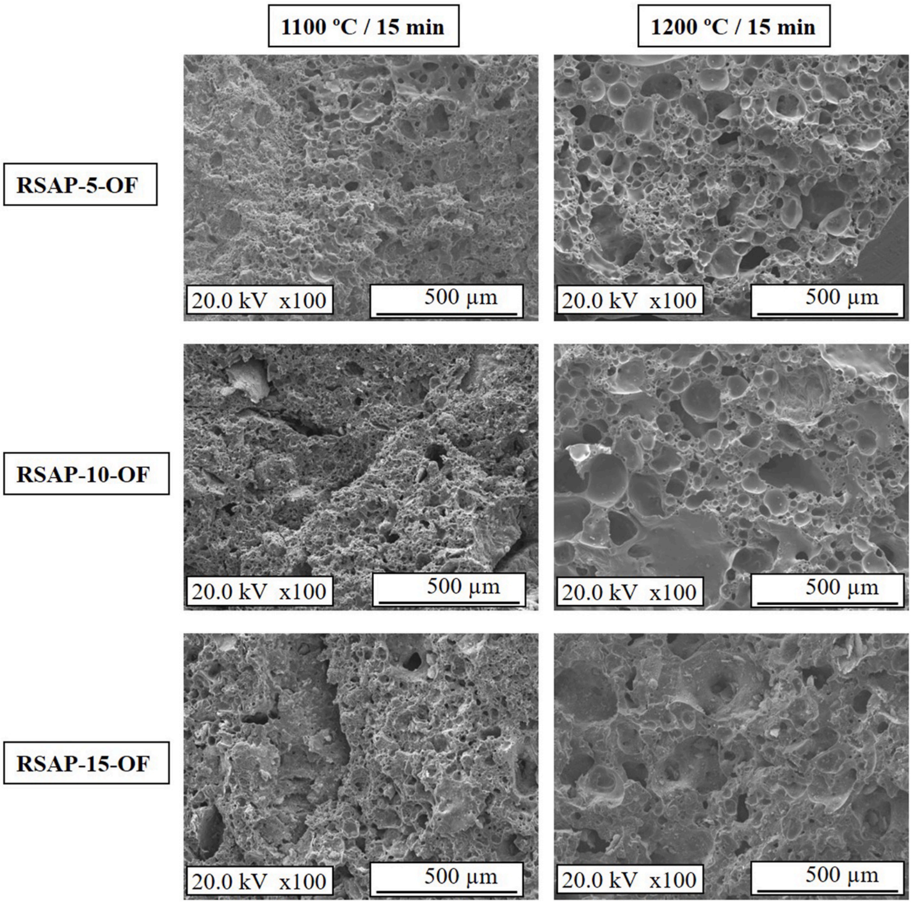

Fig. 9. FESEM observations of a cross-section of samples of the expanded clay RSAP-5-OF, RSAP-10-OF and RSAP-15-OF fired at 1100° and 1200 °C for 15 min.

release from the volatilization of the graphite incorporated in the ceramic body through the OF waste (Farias et al., 2017; Martinez-Garcia et al., 2021). Hercynite likely results from the interaction of Al_2O_3 released by the thermal decomposition of muscovite (Moore et al., 1999) with FeO generated from the reduction of magnetite.

Fig. 8 shows the X-ray diffractograms of the RSAP-15-OF composition fired in the 1000–1200 °C temperature interval. In the samples treated at 1000 °C, in addition to the quartz and hercynite phases identified at 1200 °C, magnetite (Fe_3O_4) is also detected.

Fig. 9 shows FESEM images of a cross section of samples of the expanded clays RSAP-5-OF, RSAP-10-OF and RSAP-15-OF fired at 1100 °C and 1200 °C for 15 min. The microstructure is characterized by the presence of rounded pores of variable size, whose size depends largely on the temperature at which the expansion occurred, such that the pores developed at 1200 °C are larger than those that originated during the expansion of the samples at 1100 °C. The percentage of organic fraction waste in the aggregates also influences the porosity. Thus, the size of the pores seems to increase with the content of in the expanded clay. Both effects corroborate the volumetric expansion values in Table 2.

Fig. 10 shows micrographs of cross-sections of samples of the different formulations of expanded clay heated at 1200 °C for 15 min. Increasing the percentage of the organic fraction results in a smaller number of pores but a larger pore size. The incorporation of an organic fraction content higher than 15% promoted the formation of liquid phases that filled the pores and decreased the porosity. This result agrees with the expansion study.

Table 3 shows the EDS analyses performed on the cross-sections of the expanded clay samples heated at 1100 °C for 15 min. The major component, SiO_2, is a characteristic oxide of the clay composition and decreases significantly as the percentage of waste in the expanded clay increases. Moreover, a significant increase in the amount of metal oxides (MnO and ZnO) incorporated in the composition of the expanded clay through waste was observed.

Fig. 11 shows micrographs taken from a cross-section of samples of the expanded clay RSAP-5-OF fired at 1200 °C for 15 min. At high magnification, the ceramic matrix can be seen to be covered with globular aggregates. Digital X-ray mapping images showing the distributions of iron (Fe), antimony (Sb), cobalt (Co), copper (Cu), nickel (Ni) and chromium (Cr) ions indicate that these aggregates could correspond to intermetallic compounds, which are not detected in the XRD study due to their low content in relation to the total mass of the expanded clay sample. These aggregates are mainly formed by Fe and Sb; therefore, they can correspond to an Fe/Sb alloy with a minor percentage of the other metals.

3.1. *Life Cycle Assessment (LCA)*

3.1.1. *Functional unit*

Since the main objective is to study the inclusion of the OF from alkaline battery recycling as a secondary raw material in the production of LECAs, the functional unit established was the incorporation of 1000 kg of waste (OF) into the industrial manufacturing process of LECA. These 1000 kg of OF were considered to represent a percentage by weight of 5, 10 and 15 of the total amount of raw materials (RASP + OF). These three mixtures were assumed to be the *proposed scenarios* in this LCA study (Fig. 4b), and were compared with industrial processes using only natural clay as the raw material, considered as the *state-of-the-art scenarios* (Fig. 4a).

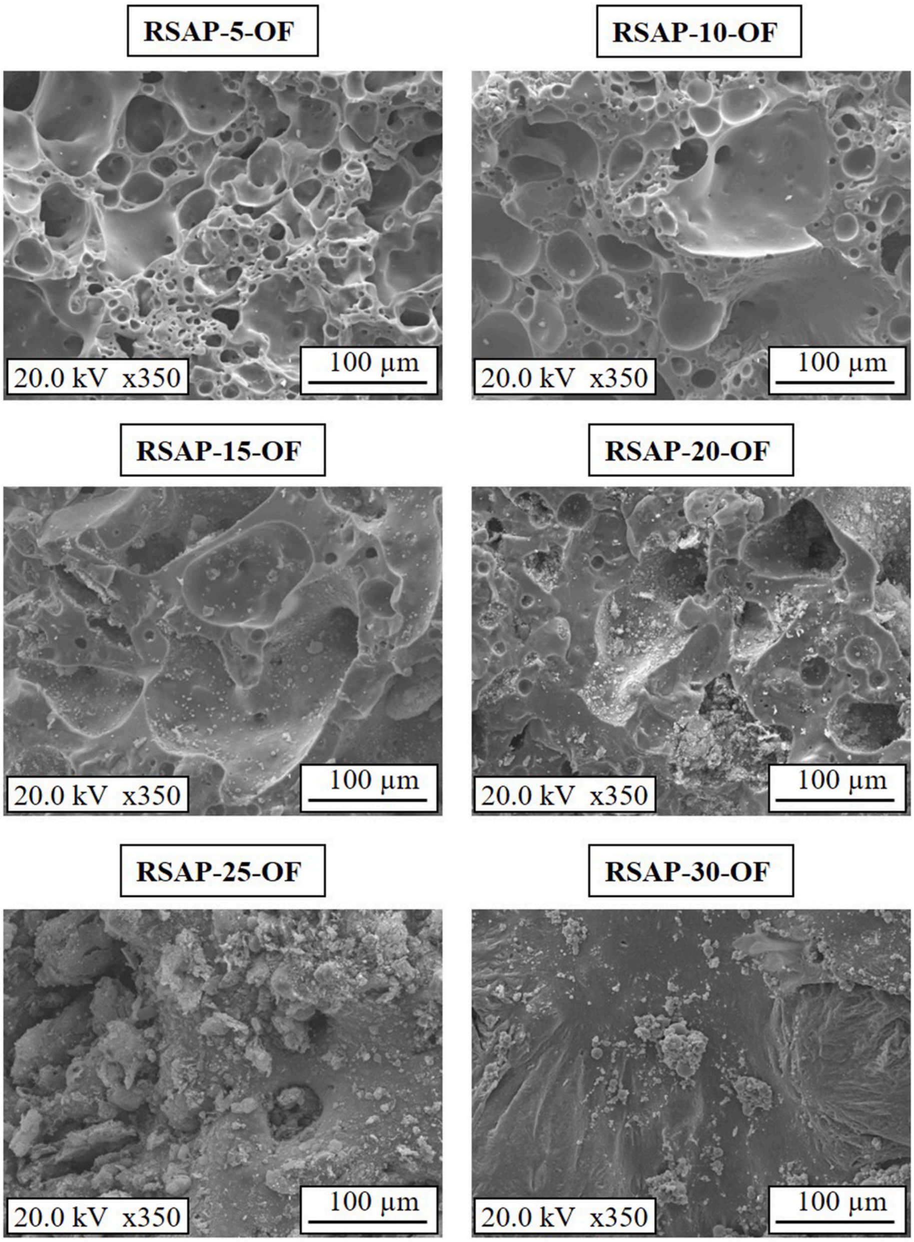

Fig. 10. FESEM observations of a cross-section of samples of the expanded clay formulated with different percentages (5–30%) of waste and fired at 1200 °C for 15 min.

Table 3
Chemical composition (wt.%) by EDS analyses performed on the cross-section of expanded clay obtained with different percentages of, and fired at 1100 °C for 15 min.

	RSAP-5-OF	RSAP-10-OF	RSAP-15-OF	RSAP-20-OF	RSAP-25-OF	RSAP-30-OF
MgO	1.20	1.59	1.28	1.54	1.82	2.44
Al_2O_3	21.91	22.23	21.52	19.88	22.63	22.08
SiO_2	48.64	44.88	46.23	45.37	36.49	26.47
K_2O	4.49	4.57	4.93	4.50	3.34	3.18
CaO	2.54	1.94	1.90	1.85	1.71	2.09
TiO_2	1.23	1.08	1.15	1.19	1.94	1.25
MnO	2.97	4.20	5.62	6.48	11.90	14.70
FeO[a]	12.29	13.38	12.27	13.93	14.74	15.84
ZnO	3.63	5.02	4.48	5.05	4.76	10.53
Minoritary oxides	1.08	0.77	0.33	0.06	0.00	0.69

[a] Total iron oxide expressed as FeO.

3.1.2. Life cycle inventory analysis

In the proposed scenarios where the OF are included, the quantities of clay to be extracted and transported are lower compared to the equivalent processes that yield the same kilograms of LECA but produced solely from natural raw materials. The same distance of 55 km was assumed for waste transportation, both from the waste producer to the LECA manufacturing facilities and to the incineration plant.[1] The OF can be incorporated into the grinding step; however, this inclusion affects only the subsequent firing stage, where the needed amount of petroleum coke is reduced due to the calorific energy generated by the combustion of waste (Table 4). The firing temperature considered for LCA was 1200 °C.

Although several studies have addressed the heating value of distinct

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[1] Based on real waste producer-incinerator distance, and to a LECA manufacturer in Spain context.

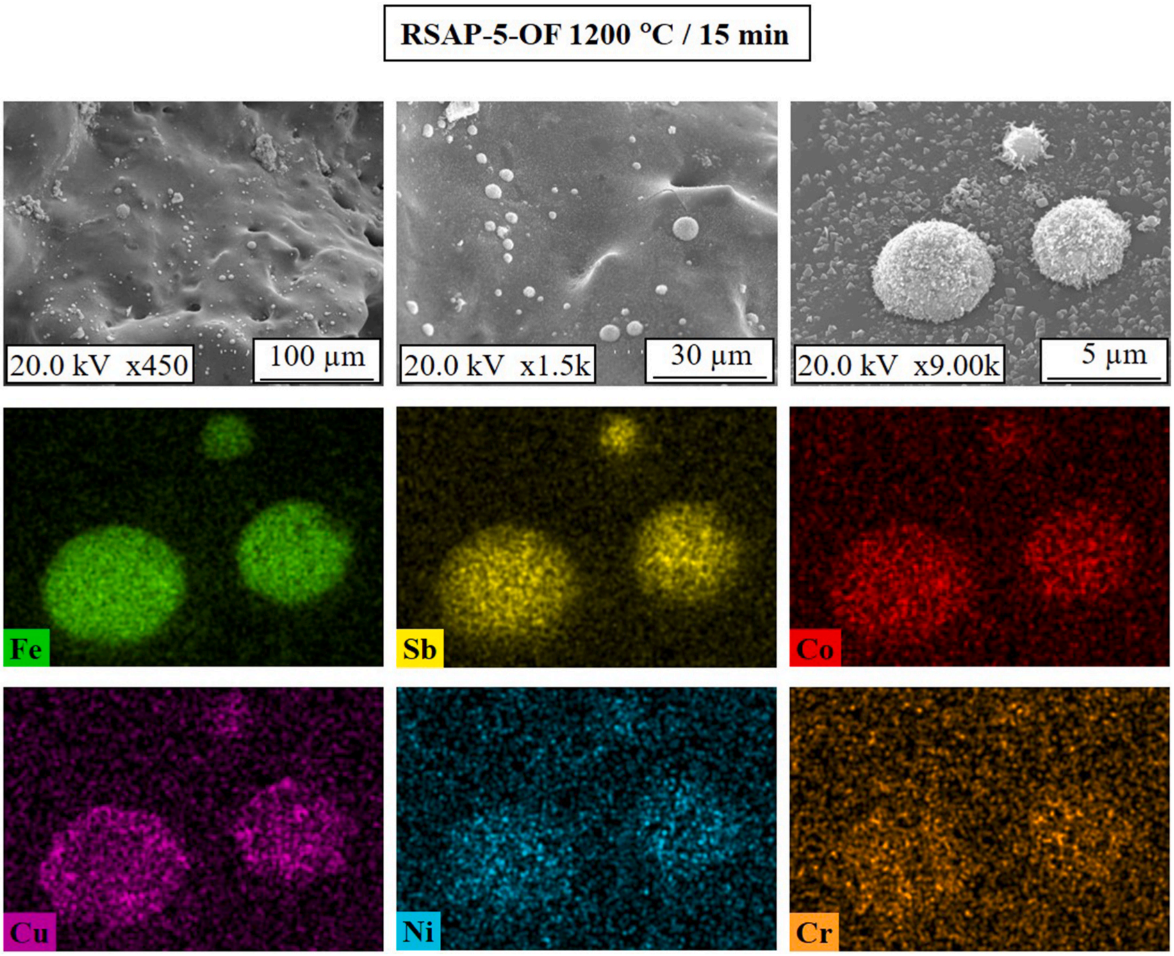

Fig. 11. Micrographs and digital X-ray mapping images taken on a cross-section of the RSAP-5-OF expanded clay samples fired at 1200 °C for 15 min.

Table 4
Energy and material inputs required for each scenario of LECA manufacturing (1200 °C).

	RSAP-5-OF	CLAY-5	RSAP-10-OF	CLAY-10	RSAP-15-OF	CLAY-15
Clay (kg)	19000	20000	9000	10000	5666.7	6666.7
OF (kg)	1000	0	1000	0	1000	0
Water (kg)*	3654.5	3654.5	1827.3	1827.3	1218.2	1218.2
Oil (kg)*	181.8	181.8	90.9	90.9	60.6	60.6
LDPE packaging film (kg)*	100.0	100.0	50.0	50.0	33.3	33.3
Petroleum coke (MJt^{-1})[a]	49135.0	49636.4	24343.3	24818.2	16096.9	16545.5
Electricity (kWh^{-1})[b]	920.2	890.9	474.8	445.5	326.3	297.0

*Their values are not affected by the addition of waste.
[a] Supplementary info, Table S1.
[b] Supplementary info.

components of alkaline batteries (Xará et al., 2005; Almeida et al., 2006), it is important to note that in these studies, the disassembly of the batteries was carried out manually. Consequently, the fractions obtained differ significantly from those produced by an industrial alkaline battery recycling process. Given the substantial variation in the composition of the resulting OF in the literature, their heating value was estimated in this study based on experimental data (ATD results are provided in the Supplementary Information).

Unlike the residue included in the reference study (Quina et al., 2020), the OF derived from alkaline batteries is classified as non-hazardous waste (Commission of the European Communities, 2010). The main source of pollutants emitted by the LECA industry comes from kiln firing, while the emissions from the other process steps remain invariable. The amount of CO_2 emitted by the OF, regardless of whether it was incinerated or included in the LECA industrial process, was calculated via thermogravimetric analysis (TG) (see the Supplementary Information). Considering that approximately 4% of the final porosity of LECAs is closed, the incorporation of the OF results in a decrease in the amount of CO_2 released. The emissions for the different scenarios studied were calculated based on the firing energy (MJ/t) needed to process the functional unit of the OF.

In the LECA manufacturing process including the OF waste, it is assumed that the avoided electricity generation was supplied by the Spanish electrical grid (year 2022). Another approach considers the calcination of clay as a thermal process with an efficiency ranging from 50 to 70% (Hanein et al., 2022). Both extreme scenarios were examined in this study. Table 4 collects energy and materials required by each scenario studied in this work.

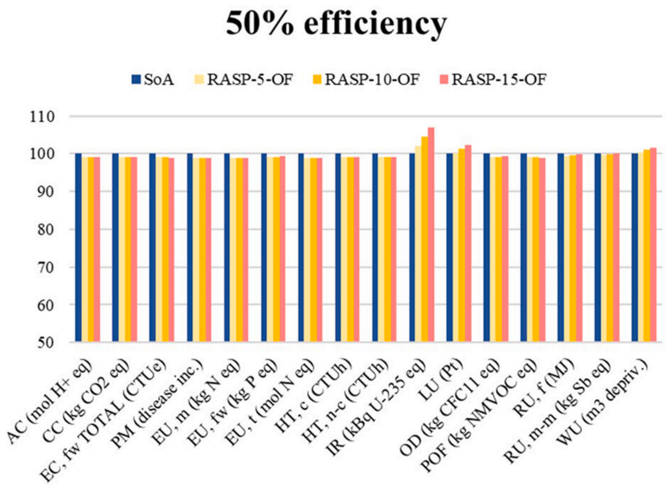

Fig. 12. Comparative environmental impacts (% variation) of the different LECA manufacturing scenarios, considering a 50% efficiency of the thermal calcination step.

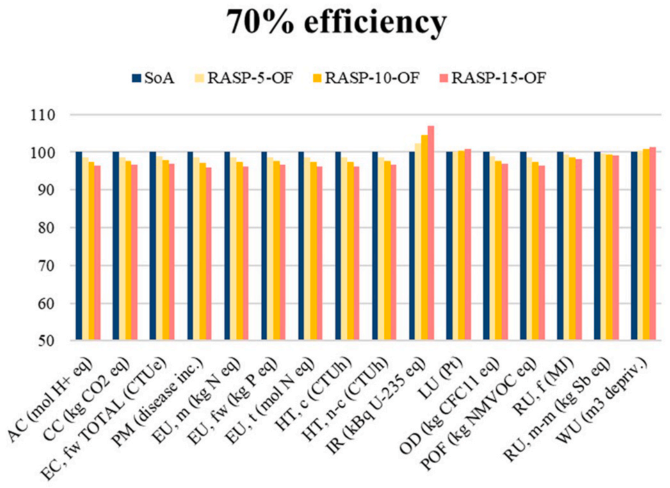

Fig. 13. Comparative environmental impacts (% variation) of the different LECA manufacturing scenarios, considering a 70% efficiency of the thermal calcination step.

3.1.3. *Life cycle impact assessment*

The environmental impacts of all the scenarios calculated for a thermal efficiency of the firing step of 50% are collected in Table S3. Fig. 12 illustrates the main impact categories within the *EF 3.1 Method.* There are three of them (IR, LU and WU) where the incorporation of OF results in slight environmental performance worsening. For the remaining categories, there are minor improvements, and they are independent of the percentage of waste included. When a thermal efficiency of 70% was considered (Fig. 13, Table S4), the slight worsenings in IR, LU and WU remained the same as in the 50% efficiency scenario. However, for the rest of the categories, the greater the amount of waste that is incorporated, the better their environmental performance.

In any case, these minor deviations do not exert a substantial impact from an environmental standpoint. This implies that although the addition of from alkaline batteries does not significantly improve the environmental parameters of LECA production, it does not worsen the process. The most important advantage of incorporating OF as a secondary raw material lies in the heightened recycling efficiency after the end of life of alkaline batteries, which approaches nearly 100%. Furthermore, this approach also avoids waste incineration. Finally, as the electricity deficit resulting from not incinerating OF in the production of LECA is compensated by the electricity grid, the greater the contribution of renewables to the electricity mix is, the more favourable the environmental performance of the entire industrial process.

From an economic perspective, the cost of natural clay is approximately 20 €/tonne, and the cost of the OF management is approximately 160 €/tonne. For the LECA manufacturer, the greater the incorporation of the OF is, the greater the savings. In the case of the battery waste manager, the economic benefits will be more substantial.

The results obtained in this study demonstrate the potential of the organic fraction from battery recycling as a bloating agent in the preparation of LECAs. However, to confirm the feasibility on an industrial scale, it will be necessary to upscale the process to a pilot plant. This step will allow for a more accurate assessment of operational variables and optimisation of production conditions. Furthermore, future applications of the produced LECAs should be investigated, particularly in the manufacturing of lightweight concretes. These materials offer significant advantages in terms of weight reduction and improved thermal and acoustic insulation, which could expand their use in sustainable construction.

4. Conclusions

The results of this study allow us to conclude that the organic fraction of alkaline batteries is a suitable material for producing expansion during the firing of clay materials; therefore, it can be used as an expansion agent in the manufacture of LECAs. In particular, lightweight ceramic materials manufactured with the addition of 5–15 wt% of organic fraction to clay material and heated at 1200 °C show density (0.65–0.75 g/cm^3) and compressive strength (1.34–1.39 MPa) values in the range of those of commercial expanded clays. Moreover, it should be noted that for lower temperatures, i.e., 1000 and 1100 °C, the values of these technological properties are even greater than those of commercial aggregates.

The three scenarios resulting in more similarities to commercial LECAs (5, 10 and 15 wt% OF, 1200 °C) were evaluated by means of Life Cycle Assessment. This is the first time that this type of residue has been included in LECA manufacturing; consequently, that an environmental study was carried out. The LCA results indicated no significant improvement or worsening effects in most of the impact categories evaluated. However, notable enhancements in the recycling efficiency of alkaline batteries could be achieved.

CRediT authorship contribution statement

Maximina Romero: Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization. **Raquel Casasola:** Writing – original draft, Visualization, Methodology, Formal analysis. **Isabel Padilla:** Writing – review & editing, Visualization. **Juan Manuel Pérez:** Writing – review & editing, Resources, Funding acquisition. **Jose-Luis Gálvez-Martos:** Writing – review & editing, Methodology, Formal analysis. **Manuel Contreras-Llanes:** Writing – review & editing, Visualization. **Aurora López-Delgado:** Writing – original draft, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

This work was funded by the Grant MAT 2017–83025–R supported by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe”. The authors thank P. Díaz and E. Martín for technical assistance. Envirobat España S.L. is also acknowledged for supplying the organic fraction of alkaline batteries sample.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2024.143422.

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