

Proceeding Paper

# Lightweight Geopolymer Composites: The Impact of the Aggregate <sup>†</sup>

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**Abstract:** In this work, lightweight geopolymer composites were produced by varying the content of expanded perlite and geopolymer spheres, used as aggregates. Firstly, highly porous geopolymer spheres containing mostly red mud as the solid precursor were produced, which leads to the valorization of significant amounts of this metallurgical waste. Then, the incorporation of each aggregate in the slag matrix demonstrated that the geometric density, compressive strength, and thermal conductivity of the geopolymer composites decrease when their content increases. Composites with low density (0.8 g/cm<sup>3</sup>) and low thermal conductivity (0.130 W/m K) were produced by using the expanded perlite. However, the sphere-containing composites showed higher specific strength and good thermal insulation properties. The results show an interesting potential of using a waste-derived aggregate, synthesized at much lower temperatures compared to expanded perlite, addressing the demand for developing novel energy efficient materials.

**Keywords:** slag; expanded perlite; geopolymer spheres; lightweight material; thermal conductivity

## 1. Introduction

The production of ordinary Portland cement (OPC)-based concrete is responsible for a large amount of energy consumption, in addition to a very high share of the anthropogenic CO<sub>2</sub> emission (~8%), which is one of the major causes of climate change. Besides this, the energy inefficiency stemming from the heating and cooling needs of the building also raises concerns regarding sustainability in the building sector [1]. In this context, there is an urgent need for alternative and highly efficient new materials with a lower carbon footprint. Geopolymers emerge as one of the most promising alternatives due to their lower embodied CO<sub>2</sub>, but also due to the possibility of using industrial wastes as precursors instead of non-renewable raw materials [1]. The production of lightweight and thermal insulating geopolymer concrete is a particularly interesting approach to increase the energy efficiency of buildings, as these materials can mitigate the energy losses [2,3]. One of the common routes involves incorporation of natural (e.g., cork [4]) or synthetic (e.g., expanded polystyrene, crumb rubber [5,6]) lightweight aggregates that ensure weight reduction. As the construction industry is striving to minimize consumption of virgin resources and precursors derived from fossil fuels, the production of aggregates from wastes or industrial by-products is given priority. In line with the above, highly porous red mud-based geopolymer spheres were synthesized in this work and used as lightweight aggregates to produce low density composite materials. Red mud is a by-product produced in large amounts during alumina production (0.8–1.5 tons of red mud per ton of alumina), which is considered an environmental hazard [7]. Then, the mechanical, thermal, and physical properties were determined to infer the influence of geopolymer spheres' incorporation content on the produced composites using slag as a binder. A comparison with a commercial and



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non-renewable lightweight aggregate was also performed, in this case by using expanded perlite. Geopolymer mortars containing expanded perlite have been proven to produce materials with better fire resistance and higher thermal insulation than siliceous sand [8].

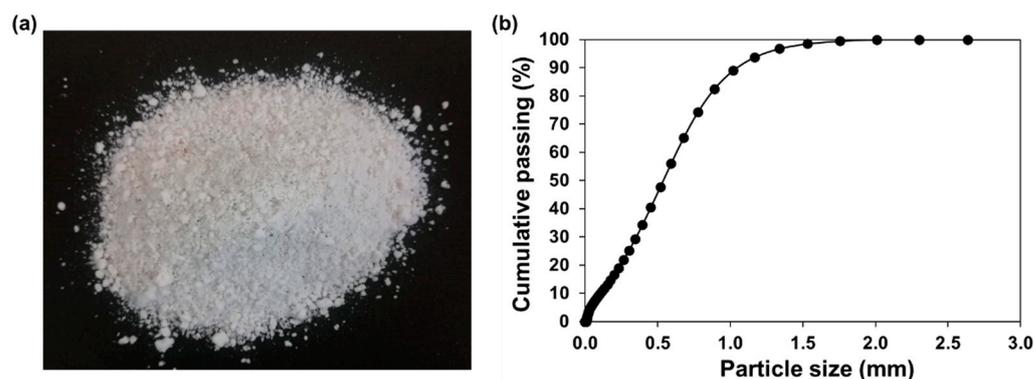
## 2. Materials and Methods

### 2.1. Materials

The porous geopolymer spheres, to be used as synthetic lightweight aggregate, were produced using two solid precursors: red mud (RM), supplied by a bauxite mining company from Greece, and metakaolin (MK) (Argical™ M1200S from Univar®, Seattle, WA, USA). Prior to use, RM was milled and sieved to attain a particle size below 75 µm, while MK was sieved to reach a particle size below 63 µm. The chemical composition of RM (Table 1) determined via X-ray fluorescence (XRF) shows that this waste is an iron-rich material (41 wt.%) with a low silica and alumina content. For this reason, MK was employed to adjust the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. To perform the chemical activation of these solid precursors, a mixture of 100 g of industrial grade sodium silicate solution (Chem-Lab, Belgium) and 13.22 g of sodium hydroxide (ACS reagent, 97%; Sigma Aldrich, Saint Louis, MO, USA) were used. Sodium dodecyl sulfate (SDS) and polyethylene glycol (PEG 600) were supplied by Sigma Aldrich to be used as a pore foaming agent and consolidation medium of the geopolymer spheres, respectively. For the geopolymer composites synthesis, the main solid precursor in the binder's production was a commercial slag (Koranel®, Metallo, Beerce, Belgium) activated via an alkaline solution consisting of a mixture of 100 g of potassium silicate (K40, Quimialmel, Albergaria-a-Velha, Portugal) and 15.25 g of potassium hydroxide (85%; PanReac AppliChem, Castellar del Vallès, Spain). Expanded perlite (Figure 1a), with a geometric density of 0.11 g/cm<sup>3</sup> and particle diameter (D50) of 0.537 mm (Figure 1b), was used as a natural lightweight material and supplied by a Greek company.

**Table 1.** Chemical composition from XRF of metakaolin (MK), red mud (RM), and slag.

Oxides (wt.%)	MK	RM	Slag
SiO <sub>2</sub>	54.40	9.20	26.92
Al <sub>2</sub> O <sub>3</sub>	39.40	18.19	8.36
CaO	0.10	9.12	3.04
K <sub>2</sub> O	1.03	0.12	0.16
Fe <sub>2</sub> O <sub>3</sub>	1.75	40.66	51.27
MgO	0.14	0.27	0.93
Na <sub>2</sub> O	-	4.72	1.97
TiO <sub>2</sub>	1.55	5.68	0.32
SO <sub>3</sub>	-	0.41	0.73
P <sub>2</sub> O <sub>5</sub>	0.06	0.11	0.71
MnO	0.01	0.05	0.77
LOI	2.66	10.71	0.08



**Figure 1.** (a) Expanded perlite aggregate and its (b) particle size distribution.

## 2.2. Synthesis of the Geopolymer Spheres

The geopolymer spheres were prepared following the experience from previous investigations [9], in which 31 g of solid precursors (55 wt% of RM and 45 wt% of MK) were chemically activated with an alkaline solution (30 g) and distilled water (8.3 g). A planetary mixer was used to mix the precursors and the activator for 5 min. Then, the foamed slurry was obtained by adding the SDS (0.9 g) to the slurry and mixing it for 2 min. Finally, the geopolymer spheres were synthesized through the suspension solidification method by injecting the foamed slurry in a polyethylene glycol medium, which was maintained under the bath temperature of  $80 \pm 5$  °C. After collecting the spheres, they were washed with water and cured in an oven at 40 °C for 24 h. Afterwards, the geopolymer spheres were cured for 28 days at room temperature.

## 2.3. Synthesis of the Geopolymer Composites

For the lightweight geopolymer composites preparation, firstly, the slag was activated with the potassium hydroxide solution with a liquid-to-solid ratio of 0.684. After mixing for 1 min, the lightweight aggregate was incorporated into the activated slag for 2 min. The volume ratios for each lightweight aggregate and the binder were firstly evaluated using preliminary tests. These tests showed that 80 vol.% and 85 vol.% were the maximum amount of expanded perlite and geopolymer spheres that could be added to the matrix, respectively, without disintegration of the composites. Three different compositions varying the amount of expanded perlite (70, 75, 80 vol.%) and other three varying the amount of geopolymer spheres (75, 80, 85 vol.%) were produced. Reference specimen was also produced without the addition of aggregates. The pastes were transferred to steel molds ( $4 \times 4 \times 4$  cm<sup>3</sup>), sealed to maintain the humidity, and cured for 24 h at room temperature. Then, the cubic specimens were removed from the molds and cured at room temperature until the 28th day.

## 2.4. Materials Characterization

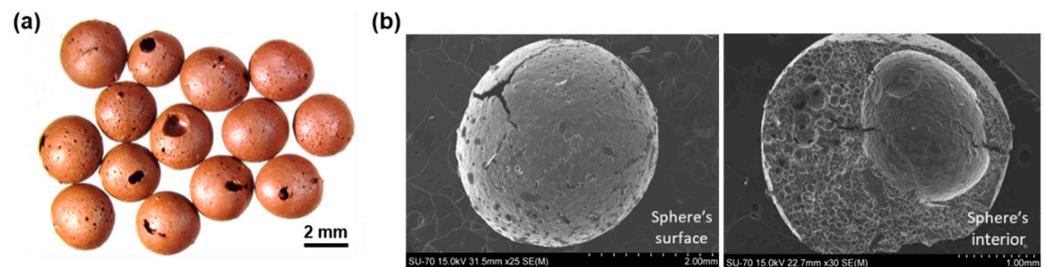
The chemical composition of the solid precursors was determined via X-ray fluorescence (XRF- Philips X'Pert PRO MPD spectrometer, Malvern Panalytical, Malvern, UK). The morphology and porosity of the spheres were examined using an optical microscope (Nikon, H550S, Tokyo, Japan). The particle size distribution of expanded perlite was conducted using laser diffraction in the dry mode (HORIBA scientific LA-960V2, Kyoto, Japan). Scanning electron microscopy (SEM—Hitachi SU 70; energy dispersion spectroscopy—EDS Bruker) was also used to characterize the microstructure of the spheres. The geometric density was calculated via the ratio of dry mass to volume using three cubic specimens ( $4 \times 4 \times 4$  cm<sup>3</sup>) of each formulation cured for 28 days. The compressive strength of composite specimens ( $4 \times 4 \times 4$  cm<sup>3</sup>), measured 28 days after their synthesis, was performed using a Universal Testing Machine (Shimadzu AG-25 TA, Kyoto, Japan) at a 0.5 mm/min load rate in triplicate per batch, following the standard EN 1015-11:1999 [10]. The thermal conductivity was measured on three cubic specimens ( $4 \times 4 \times 4$  cm<sup>3</sup>) of each composition by using a heat flow meter apparatus following the ASTM C518-04 standard [11], where the sample is placed between two parallel plates, with a constant temperature gradient of 15 °C.

# 3. Results and Discussion

## 3.1. Geopolymer Spheres Characterization

Figure 2a shows the optical micrographs of RM-containing geopolymer spheres. The spheres have a spheroidal shape and narrow size distribution, with an average diameter of  $2.9 \pm 0.8$  mm. The SEM micrographs of the geopolymer spheres' surface and interior microstructure are shown in Figure 2b. The spheres reveal a homogeneous smooth surface with small-sized pores, while their interior shows the presence of a large-sized and closed pore surrounded by mostly small-sized closed pores and a few open pores. The geometric

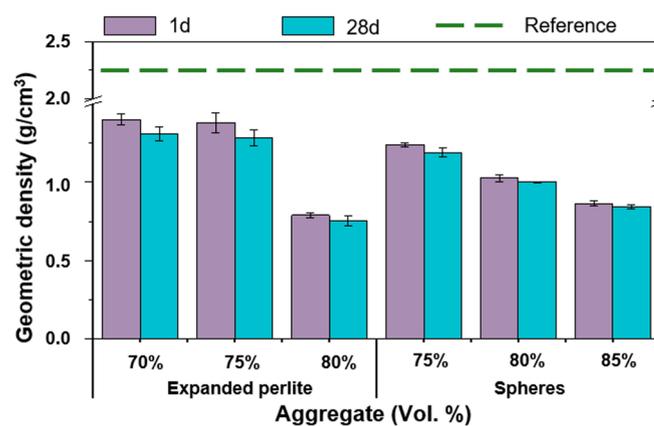
density of geopolymer spheres was  $0.57 \text{ g/cm}^3$ , with this value endowing their use as a lightweight aggregate.



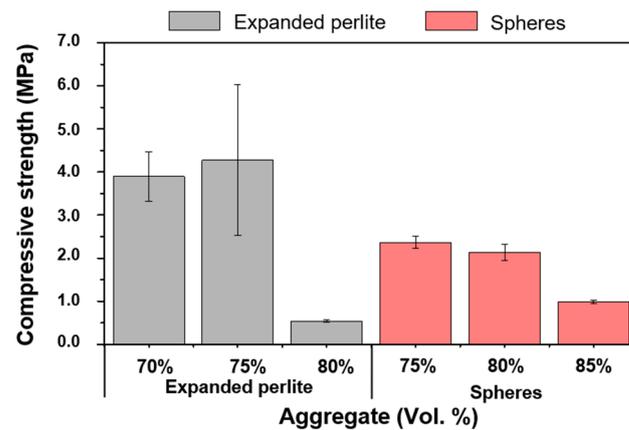
**Figure 2.** (a) Optical microscopy and (b) SEM micrographs of the red mud-based geopolymer spheres.

### 3.2. Geopolymer Composites Characterization

The geometric density of the geopolymer composites is reduced with the addition of both lightweight aggregates, reaching values below  $1.40 \text{ g/cm}^3$  in all studied composites, which represent a reduction of at least 39% in comparison with the reference specimen prepared without the lightweight aggregate (Figure 3). A small density decrease is observed between the first and the twenty-eight day of cure as a result of the dehydration process during the polycondensation reaction. Noteworthy, a major reduction in the geometric density of composites is seen when increasing the amount of the aggregates, the lowest geometric density ( $0.75 \text{ g/cm}^3$ ) reached by the higher volume (80 vol.%) of expanded perlite, followed by the composite with 85 vol.% of spheres ( $0.84 \text{ g/cm}^3$ ). At 80 vol.% of aggregate, the geometric density of composite containing expanded perlite is roughly 1.3 times lower than the density with the same volume of spheres ( $1.00 \text{ g/cm}^3$ ). However, no significant difference is observed with 75 vol.% of each aggregate, even though the expanded perlite's geometric density is roughly five times lower than the density of the geopolymer spheres. This feature is attributed to the fragile nature of expanded perlite, which can be partially destroyed during the mixing step, leading to higher density values than those expected when considering the apparent density of this aggregate. In fact, this phenomenon led to specimens having heterogeneous mechanical properties, as can be observed in Figure 4.



**Figure 3.** Geometric density of geopolymer composites varying the amount of expanded perlite and geopolymer spheres (measured on the 1st and 28th day). Reference means the control specimen without addition of lightweight aggregate.



**Figure 4.** Compressive strength (MPa) of geopolymer composites varying the amount of expanded perlite and geopolymer spheres.

The mechanical performance under compression of all composites is shown in Figure 4. The compressive strength decline is more pronounced at the highest incorporation volume of the aggregates, with the lowest value for specimens composed with 80 vol.% of expanded perlite (0.5 MPa) followed by the one with 85 vol.% of spheres (1.0 MPa). Despite the small difference in their geometric densities, the composite with 85 vol.% of spheres has a compressive strength two times higher than composite containing 80 vol.% of expanded perlite. With 75 vol.% of expanded perlite, the compressive strength is approximately twofold higher than the composite using the same amount of spheres. However, the result seen for the perlite-containing composite is abnormal and should be considered with caution. These samples were heterogenous, possibly due to a partial destruction of perlite during the mixing step, and this explains the very high standard deviation of composites with 75 vol.% of expanded perlite. Nevertheless, it should be noted this feature was not observed when using higher volumes of this aggregate. Indeed, with the incorporation of 80 vol.% of aggregate, an opposite tendency occurs, where the composite with spheres has a compressive strength fourfold higher than the expanded perlite, which can be explained by its higher composite's geometric density. The specific strength of the specimens with lower densities was determined and showed the following: 80 vol.% of spheres (2.1 MPa cm<sup>3</sup>/g) > 85 vol.% of spheres (1.8 MPa cm<sup>3</sup>/g) > 80 vol.% of expanded perlite (0.7 MPa cm<sup>3</sup>/g). The high specific strength of composites containing the spheres demonstrates the interesting properties of this material, enabling their use as a lightweight aggregate in the production of low density geopolymers.

The thermal conductivity of composites drops when the content of each lightweight aggregate rises, as shown in Table 2. The lowest value of thermal conductivity (0.130 W/m K) was observed in the composite with the highest volume of expanded perlite. For the same concentration, the addition of expanded perlite generates materials with lower thermal conductivity than the use of geopolymer spheres, but it is only significantly different at 80 vol.%. These results show that thermal conductivity can be controlled by the type of lightweight aggregate and by its content. The thermal conductivity value (0.175 W/m K) of composite containing the utmost volume of geopolymer spheres validates the strategy of using them as a lightweight aggregate. Moreover, their use has sustainable advantages over expanded perlite, since spheres are synthesized at 80 °C, this being much lower than the common temperatures involved in the expansion of perlite (850–1100 °C) [12,13]. Additionally, they are mostly produced using hazardous and abundant (150 Mt/year) industrial waste, contributing not only to reduce its stockpile but also to avoid the use of virgin raw materials. The lowest value of thermal conductivity obtained here (0.130 W/m K with expanded perlite) was compared with the literature and demonstrated to be smaller than geopolymer mortars incorporating expanded perlite (0.370 W/m K) [8] and crumb rubber (0.279 W/m K) [6],

similar with the addition of waste-expanded polystyrene (0.121 W/m K) [5], but higher than those seen when using cork (0.072 W/m K) [4].

**Table 2.** Thermal conductivity (W/m K) of geopolymer composites produced with distinct expanded perlite and geopolymer spheres content.

Lightweight Aggregate	vol. %	Thermal Conductivity (W/m K)
Expanded perlite	70	0.240 ± 0.017
	75	0.215 ± 0.017
	80	0.130 ± 0.009
Spheres	75	0.234 ± 0.012
	80	0.215 ± 0.007
	85	0.175 ± 0.008

#### 4. Conclusions

Geopolymer composites were produced here using expanded perlite or geopolymer red mud-based spheres as a lightweight aggregate. The effect of their content in the composite was investigated via the mechanical, thermal, and physical properties. Results show that by increasing the aggregate amount, the compressive strength, geometric density, and thermal conductivity tend to decrease, demonstrating that these properties can be tuned considering the application envisioned. The composition containing the highest expanded perlite volume achieved the lowest value of geometric density (0.8 g/cm<sup>3</sup>) and of thermal conductivity (0.130 W/m K). Nevertheless, the use of red mud-based spheres resulted in a higher specific strength. These results suggest that this waste-derived aggregate can be a promising alternative in the development of sustainable and energy efficient geopolymer materials, also contributing to reduce the environmental impact associated with waste landfilling.

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