processes

Article

Volcanic Ash from the Island of La Palma, Spain: An Experimental Study to Establish Their Properties as Pozzolans

Leticia Presa [1,*], Santiago Rosado [1,2], Christian Peña [1], Domingo Alfonso Martín [1,2,3], Jorge Luis Costafreda [1], Beatriz Astudillo [1,2,3] and José Luis Parra [1]

1 Escuela Técnica Superior de Ingenieros de Minas y Energía, Universidad Politécnica de Madrid, 28003 Madrid, Spain
2 Fundación Gómez Pardo, Calle Alenza, 1, 28003 Madrid, Spain
3 Laboratorio Oficial para Ensayos de Materiales de Construcción (LOEMCO), Calle Eric Kandel, 1, 28906 Getafe, Spain
* Correspondence: leticia.presa.madrigal@upm.es

Abstract: The eruption of the Cumbre Vieja volcano on 19 September 2021, resulted in the deposition of large quantities of volcanic ash (VA), causing a great impact on the citizens. This work aims to study the properties of this volcanic ash as pozzolanic raw materials to establish their potential use in the development of sustainable cement. Results of chemical and technical characterization are presented. To achieve this goal, Ordinary Portland Cement (OPC) was replaced with standardized percentages of OPC/VA: 10, 25, and 40%. Characterization studies were carried out using chemical analysis of X-ray fluorescence (XRF), chemical quality analysis (QCA), pozzolanicity test (PT) at 8 and 15 days, as well as determining the mechanical strength (MS) at 7, 28, and 90 days. The results obtained by XRF and QCA established that the chemical composition of the VA corresponds to that of the natural pozzolan typical of pyroclastic genesis. The PT test showed that the analyzed samples have a marked pozzolanic nature, both at 8 and 15 days, showing a significant increase in their hydraulic reactivity. Likewise, the MS tests confirmed a continuous increase in mechanical compressive strength, which increased significantly from 7 to 90 days of curing, reaching more than 58 MPa. On the other hand, mechanical tests showed that the three types of dosages used OPC/VA: 10, 25, and 40% were equally effective, with OPC/VA formulations: 10–25% being the most effective. The results obtained in this research could be used by local industries as a guide for the correct use of the volcanic materials of this island, both for the manufacture of construction materials, such as aggregates, and to produce pozzolanic cement with low CO_2 emissions, thus having a positive impact on the environment. Finally, the great natural availability of natural VAs in the surrounding areas of La Palma could cover part of the needs for materials used in the construction and restoration of houses and infrastructures damaged during the volcanic eruption.

Keywords: volcanic ash; pozzolanicity; pozzolans; mechanical strength; cement; pyroclastic; Cumbre Vieja volcano

check for updates

Citation: Presa, L.; Rosado, S.; Peña, C.; Martín, D.A.; Costafreda, J.L.; Astudillo, B.; Parra, J.L. Volcanic Ash from the Island of La Palma, Spain: An Experimental Study to Establish Their Properties as Pozzolans. *Processes* **2023**, *11*, 657. https://doi.org/10.3390/pr11030657

Academic Editor: Slawomir Stelmach

Received: 13 January 2023
Revised: 15 February 2023
Accepted: 20 February 2023
Published: 22 February 2023

1. Introduction

The geological environment of the Canary archipelago, as well as the geological diversity of this enclave, has a practically inexhaustible source of geological resources. The island of La Palma is the second youngest of the Canarian Archipelago. Together with the island of Hierro, which is the youngest, the islands have experienced the most volcanic activity in recent years [1]. During volcanic eruptions, lava, gases, and huge amounts of pyroclastic material projected over great distances are ejected. In the last eruption of La Palma, on 19 September 2021 (Figure 1), between 8 and 9 million cubic meters of ash were expelled, according to the Instituto Volcanológico of the Canary Islands.

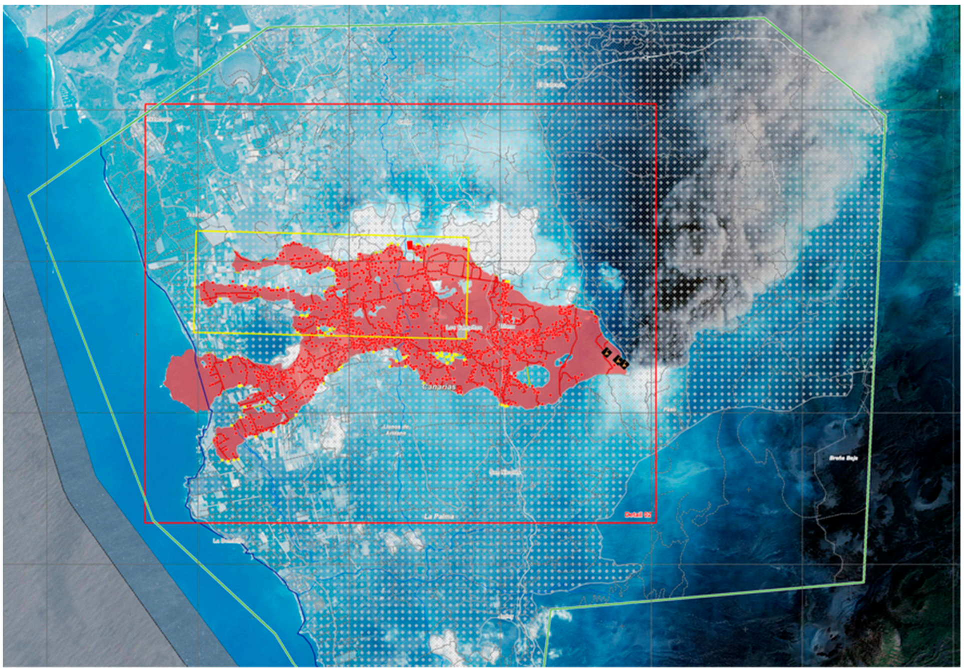

Figure 1. Image of the palm eruption by the Copernicus Emergency Management Service (European Union (2021) [2].

Pyroclastic materials from past and recent volcanic eruptions have been widely used, especially in the manufacture of aggregates, concrete, mortars, and cement [3–5]. Today, the volcanic materials of the Canary Islands are considered an invaluable geological heritage [6], including the geomorphological aspects in which they are framed. As Flores et al. [7] and Gómez-Arriaran [8] point out, the pyroclastic materials and trachytic tuffs that lie on the island of Gran Canaria, have reactive SiO_2 contents of up to 18%, thanks to which they have managed to improve the durability of the concretes by mixing these materials with polypropylene fibers, whilst also reducing the permeability of water and the corresponding diffusion of CO_2. Rodríguez and García [9] have made efficient thermal improvements in the concrete blocks currently produced in the Canary Islands, thus avoiding the traditional use of monolayer masonry in the exterior parts of buildings, creating economic and environmental advantages. Lomoschitz et al. [10] and Sánchez-Fajardo et al. [11,12] have been able to value blocks made from lapilli of basaltic origin due to their consequent reduction of the alkali-silica reaction, the improvement of their structural properties, mechanical resistance to compression, effective acoustic, and thermal insulation, as well as low density and thermal conductivity. García-González et al. [13] have carried out a detailed study of the typical volcanic materials most used in the construction industry in the Canary Islands, consisting of basalts, trachytes, phonolites, ignimbrites and pyroclasts. The above-mentioned researchers made correlations between the most common properties of these lithologies—such as volumetric, geometric, and mechanical—which permitted them to make a diagnosis of the previous behavior of the aggregates manufactured from these materials. On the other hand, other authors such as Franesqui et al. [14] have shown that, with the mixture of pyroclastic volcanic materials of basaltic origin, together with asphalt and rubber, many properties such as moisture resistance, rolling resistance and stability can be improved, making it qualitatively superior to conventional mixtures. This team of researchers [15] have also successfully employed pyroclastic materials in the construction of the non-surface layers of roads. Yanes and Del Río [16] carried out a study on the mechanical behavior and water vapor transmission properties of specimens made with pyroclastic material, to which they added standardized percentages of expanded polystyrene (EPS), resulting in a decrease in the weight of the specimens by more than 32%, compared to conventional specimens, as well as greater resistance to water vapor. Cements with added pozzolanic materials of pyroclastic origin, in addition to their pozzolanic reactivity as demonstrated by Djeunou [17], also provide resistance to sulphates and seawater [18]—a very important characteristic considering the environment of the Canary Islands. Recently, Rosales et al. [19] proved their effectiveness as a cementitious material with a fine fraction of volcanic ash from the Cumbre Vieja volcano (Spain). By using pozzolanic materials as active additions to cement, it is possible to reduce the emissions that are generated in the manufacture of cement, which accounts for about 8% [20–22] of total global CO_2 emissions.

The object of this paper is to demonstrate and establish the pozzolanic behavior of the volcanic ash ejected during the recent eruption of the Cumbre Vieja Volcano on the Island of La Palma and establish its possible use in the manufacture of pozzolanic cement, mortars, and concrete. The results presented in this paper could serve as a guide for local industries in the process of rebuilding cities affected by a volcanic eruption. On the other hand, the use of these ashes as pozzolans, as shown in this work, would make it possible to reduce CO_2 emissions generated during the cement manufacturing process.

2. Materials and Methods

2.1. Materials

Four samples of approximately 5 kg of volcanic ash (VA) from the volcanic eruption of Cumbre Vieja, on the Island of La Palma, Province of Santa Cruz de Tenerife, Canary Islands, Spain (Figure 2), were taken by the selective sampling of lithogeochemical fragments, from the large deposits formed in the piedmont of the volcano. The samples collected have amorphous, cryptocrystalline, aphyric, and conchoidal textures, with a strong tendency to fragmentation, disintegration, and friability. At the time of the sampling, they were completely dry and without moisture.

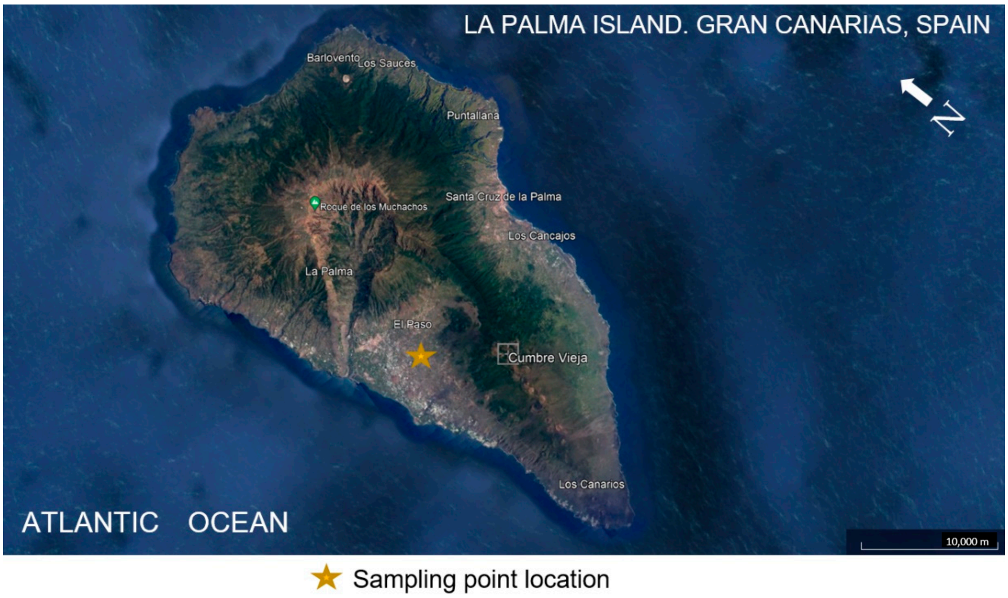

Figure 2. Map of the of the sampling point location [23].

2.2. Methods

2.2.1. Sample Preparation

To make the tests and analyses described in this work, VA samples were previously ground with a vibrating-disc mill to obtain a Blaine-specific surface of 6000 cm^2/g. This fineness is similar to that of ordinary Portland cement (OPC), which promotes more effective hydraulic reactions between volcanic ash and Portland cement; this phase of preparation of the total sample was carried out following the procedures of the Standard UNE-EN-196-6:2019 [24]. They were then mixed and homogenized according to the guidelines of Standard UNE-EN-196-7:2008 [25] to obtain a global homogeneous sample.

2.2.2. Fineness by Blaine Method

The air permeability method (Blaine method) was used to determine the fineness. Fineness was measured as a specific surface area by observing the time it takes for a fixed amount of air to pass through a compacted layer of cement of specified dimensions and porosity, as established in UNE-EN 196-6:2019 [24].

2.2.3. Real Density by Air Pycnometer (Alternative Method)

The air pycnometer method was used to determine the density. Using a known and dry mass of the material in one of the two hermetic chambers of an air-comparison pycnometer and raising the air pressures in both chambers, the volume difference was obtained, which is the volume of the material. Since its mass is known, its density was calculated by the following equation, as established by standard UNE 80103:2014 [26]:

$$\rho\left(\mathrm{g/cm^3}\right) = \frac{\mathrm{m}}{\mathrm{V}} \tag{1}$$

where:

m is the mass of dry material (g)
V is the volume difference (cm^3).

2.2.4. Chemical Composition by X-ray Fluorescence (XRF)

To determine the chemical composition of the samples, a fusion was made with lithium tetraborate in sample ratio: flux (0.3: 5.5) in PerlX'3 induction perlator (Philips). It was analyzed by Wavelength Dispersion X-ray Fluorescence Spectrometry (WDXRF) in PANalytical's ZETIUM equipment with a Rhodium tube and the Mayores program.

2.2.5. Chemical Analysis to Determine the Volcanic Ash Quality (QCA)

The chemical analysis to determine the technical quality of volcanic ash (QCA) was carried out to ascertain the pozzolan efficiency of the samples, both qualitatively and quantitatively, which ensures its use as an additional material in the process of clinkerization of pozzolanic cements. It is a technical test that was performed following the criteria established by the Standard UNE-EN 196-2:2014 [27]. The main compounds that were found in this study were the following: total SiO_2 (TS), reactive SiO_2 (RS), Al_2O_3, total CaO (TC), reactive CaO (RC), MgO, Al_2O_3, Fe_2O_3, sulfate and chloride content, as well as the insoluble residue (IR). The RS was determined by colorimetry.

2.2.6. Chemical Pozzolanicity Test (CPT)

The chemical pozzolanicity test is based on the comparison of the concentration of the calcium ion in the solution in contact with the hydrated cement with the amount of calcium ion that saturates a solution of similar alkalinity [28,29]. The solution is made of a mixture of ordinary Portland cement (OPC) and volcanic ash (VA). Its behavior was assessed at 8 and 15 days. According to Standard UNE-EN-196-5:2011 [28], the procedure used is as follows: 100 g of VA was sieved in a sieve of 150–125 µm. The retained product was ground up again to a lower granulometry. Then 20 g of the OPC:VA mixture was taken and put in 100 mL of distilled water, with an electrical conductivity of (EC) ≤ 0.5 mS/cm and a temperature of 40 °C. The sample was shaken for 20 s and left to decant for 8 and 15 days. The final solution was filtered for 30 s. The solution was cooled at room temperature. Next, the total alkalinity (TA) of the solution was determined with dilute hydrochloric acid 0.1 mol/L. Finally, the concentration in hydroxyl ions $[OH]^-$ and CaO was calculated using the following equations:

Concentration in hydroxyl ions $[OH]^-$:

$$[OH]^- = \frac{1000 \times 0.1 \times V_3 \times f_2}{50} = 2 \times V_3 \times f_2 \tag{2}$$

where:

V_3 is the volume of the 0.1 mol/L HCl solution used in the titration
f_2 is the HCl dissolution factor 0.1 mol/L.

CaO concentration:

$$[CaO] = \frac{1000 \times 0.03 \times V_4 \times f_1}{50} = 0.6 \times V_4 \times f_1 \quad (3)$$

where:

V_4 is the volume of the Ethylenediaminetetraacetic acid (EDTA) solution used in titration (mL)
f_1 is the factor of EDTA dissolution.

2.2.7. Mechanical Strength Tests at 7, 28, and 90 Days

To establish the mechanical properties, standardized mortar specimens were developed according to UNE 196-1 [30] made up of OPC:VA with three different proportions of replacement of ordinary Portland cement (OPC) by volcanic ash (VA). The mortar specimens were studied at normalized ages of 7, 28 and 90 days. The water–cement ratio (W/C) was 0.5, and the cement-to-fine aggregate ratio (C/FA) was 0.33 in all specimens. The proportions of ordinary Portland cement (OPC) and volcanic ash (VA) in each specimen were as follows: OPC/VA: 90/10%, OPC/VA: 75/25%, and OPC/VA: 60/40%. Additionally, specimens composed only of Portland cement (REF: 100%) were made to monitor the mechanical behavior of the remaining specimens in the different time periods of the tests. Table 1 shows the specimens made with mixed mixtures, the reference specimen and the various proportions of materials used in the dosages.

Table 1. Design of the dosages of the mortar specimens used in this study.

Materials	**Designation of Mortar Specimens**			
	REF [1]	**M-1**	**M-2**	**M-3**
Substitution Rate (%)	**0%**	**10%**	**25%**	**40%**
OPC [2] (g)	450	405	337.50	270
VA [3] (g)	0.00	45	112.50	180
Sand (g)	1350	1350	1350	1350
DW [4] (%)	12.5	12.5	12.5	12.5
DW (g)	225	225	225	225
Total (g)	2025	2025	2025	2025

[1] Mortar specimen used as a reference (REF); [2] OPC: Ordinary Portland cement; [3] VA: Volcanic ash; [4] DW: Distilled water.

All the stages and test methodologies applied at this point are those that correspond strictly to Standard: UNE-EN-196-1: 2018 [30]. In every case, 3 batches of specimens with dimensions of 40 × 40 × 160 mm were made from each mixture, which was tested by the three-point loading method to determine the flexural strength, loading the lateral faces of the specimens at a speed of about 2400 N/s, for the compressive strength test.

2.2.8. Resistance Activity Index

The resistant activity index (RAI) is the percentage of minimum strength required by the UNE-EN 196-1:2018 Standard [30]. For cement with 25% substitution, the compressive strength should be greater than or equal to 75% of the reference value at 28 days of curing.

This concept was exported for all ash proportions of this study, and the RAI was calculated at 10, 25, and 40% substitutions at all ages tested. It was assumed that the compressive strength of cement with substitutions should be at least 90, 75, and 60% (recommended value), respectively, in comparison with the reference cement.

3. Results

3.1. Fineness and Density

Table 2 shows the results of the fineness and density of the cement and the VA. The density values obtained are within the expected range [31–33]. The difference in densities between the cement and the volcanic ash means that the density of the mortar will decrease as the percentage of substitution increases.

Table 2. Results of the fineness and density.

	Fineness (cm^2/g)	**Density (g/cm^3)**
Cement	3962	3.14
Volcanic Ash (VA)	6000	2.86

As for the fineness, the value of the ashes is higher than the reference cement, but it is within the range of the values of other studies [34–37].

3.2. Chemical Composition Results by X-ray Fluorescence (XRF)

Table 3 shows the results of the chemical composition by X-ray fluorescence (XRF) obtained from the analysis of a sample of VA, as is the object of this study. The values obtained, mainly those SiO_2, Al_2O_3 y CaO, show a similar result to those obtained by Siddique [38,39], Alraddadi and Assaedi [40] and Játiva et al. [41] in their studies on natural pozzolans of volcanic and volcano-sedimentary origin. The contents of Fe_2O_3 y MgO indicate a composition of mostly ferromagnesian, preferably basaltic, while CaO and Na_2O construe a chalcoalkaline chemism of the samples. However, one aspect to highlight is the low or almost zero value of the loss on ignition (LOI), which accentuates the differences between the pozzolans of zeolitic [42] and bentonite origin [43]. This kind of composition, mostly silica, aluminium, iron, calcium, and magnesium, indicates the presence of typical volcanic ash minerals such as albite, hematite, magnetite, anorthite, augite, diopside, and quartz (the existence of an amorphous phase should also be considered) [19,41].

Table 3. Results of chemical analyses obtained by X-ray fluorescence + ICP/AES (Sodium).

Compounds in % Weight										
SiO	**Al_2O_3**	**Fe_2O_3**	**CaO**	**TiO_2**	**MnO**	**K_2O**	**MgO**	**P_2O_5**	**Na_2O**	**LOI ***
43.4	13.4	13.5	10.9	3.60	0.205	1.47	8.10	0.756	3.77	−0.53

* Loss on ignition.

3.3. Results of the Chemical Analysis to Determine the Quality of Volcanic Ash (QCA)

Table 4 shows the results of the chemical analysis made to determine the quality of volcanic ash (QCA). The calculated contents of total SiO_2 and total CaO, Al_2O_3, MgO, Fe_2O_3, and loss of ignition (LOI) are comparatively close to those shown in Table 3, which confirms the effectiveness of both analyses. The values obtained from the calculation of the relationship SiO_2/(CaO+MgO) show a balanced proportion of these compounds in the sample studied. None of the values shown in Table 4 disagrees with the requirements indicated by Standard UNE-EN 196-2-2014 [27].

3.4. Results of the Chemical Pozzolanicity Test (CPT)

Figure 3 shows the results of the chemical analysis of pozzolanicity performed on the mixture of ordinary Portland cement (OPC) and volcanic ash (VA), with a dosage of OPC/VA: 25%, during a standardized period of 8 and 15 days, respectively [28]. According to Figure 3, the VA sample behaves like a typical natural pozzolan, as is seen by the position it occupies under the isothermal curve of solubility at 40 °C, which is interpreted as a high reactivity of the volcanic ash with the calcium hydroxide present in the solution. This fact confirms one of the main objectives set out in this research.

Table 4. Results of the chemical composition and pozzolanic quality of the samples studied.

Compounds	Results (%)
Total SiO_2	44.22
Reactive SiO_2	39.71
Total CaO	11.08
CaO free	0.0
Reactive CaO	10.31
Al_2O_3	13.85
MgO	7.3
Fe_2O_3	14.34
Sulphates	0.0549
Chlorides	0.062
[1] IR	10.29
[2] LOI	0.02
$SiO_2/(CaO+MgO)$	2.5

[1] Insoluble residue; [2] Loss of ignition.

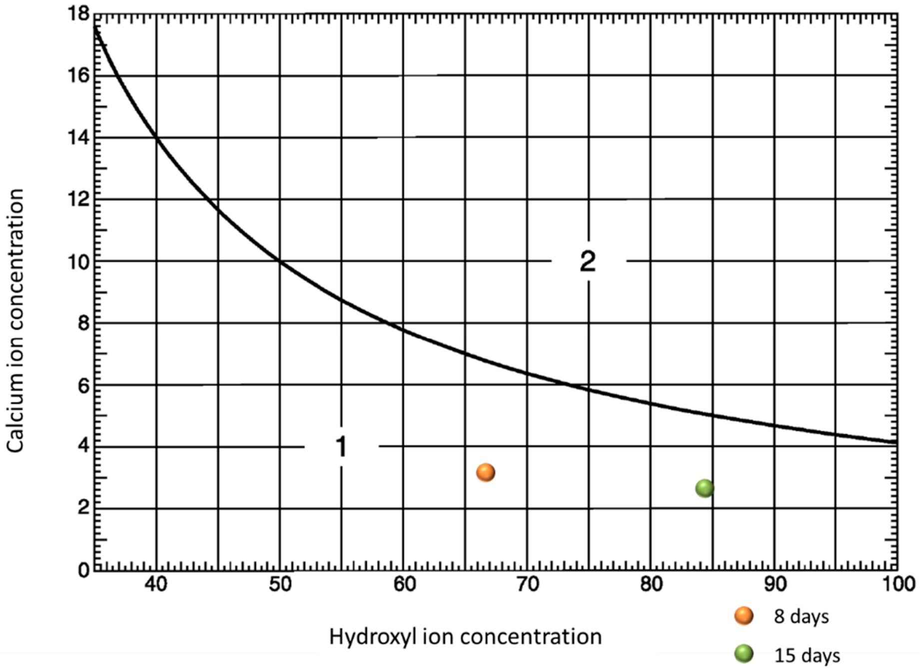

Figure 3. Graphs of concentration of $Ca(OH)_2$ and hydroxyl ions (mmol/L), depicting the behaviour of pozzolanic reactivity at 8 and 15 days.

These results are not in concordance with the results published by Rosales et al. [19], in which pozzolanicity values above the solubility isotherm are obtained. This difference may be likely due to the difference in the specific surface area of the ashes employed as cement substitution. In the present study, the ashes were milled until a Blaine value of 6000 cm^2/g, which is a value higher than the cement (3500 cm^2/g). Because the pozzolanic property depends to a great extent on the specific surface of the material, the higher the surface area exposed, the greater the reaction will be.

3.5. Mechanical Strength Tests at 7, 28 and 90 Days

Figure 4 shows the results of mechanical flexural strength obtained from the study of OPC/VA and REF specimens at the ages of 7, 28, and 90 days. The pozzolanic reactivity of the VA is obvious, as is observed at 7 days showing that the M-1 sample visibly exceeds the reference specimen (REF); however, this trend is still seen at both 28 and 90 days, respectively, where M-1 and M-2 equal the reference value.

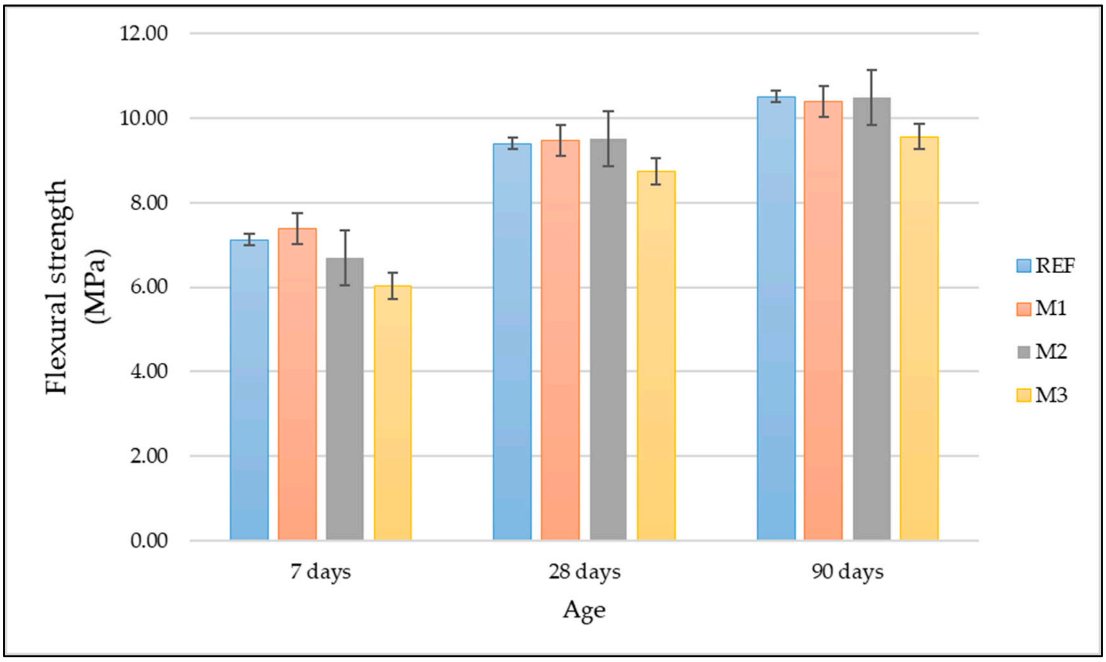

Figure 4. Results of the mechanical flexural strength test performed on the mortar specimens analyzed at 7, 28 and 90 days.

Regarding mechanical compressive strength (Figure 5), the situation is similar to that observed in Figure 2. A fact to highlight is that the values of mechanical strength determined for each specimen at 28 days exceed the minimum values indicated by the Standard UNE-EN-196-1: 2018 [30] for that same age (≥32.5 MPa), simultaneously providing "normal" and "high" type resistances.

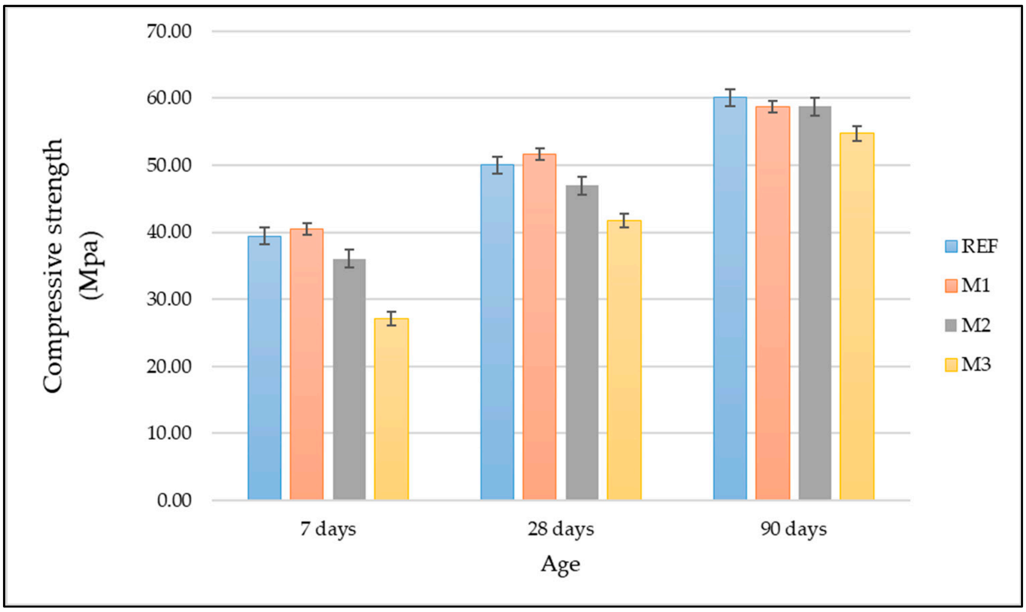

Figure 5. Results of the mechanical compressive strength test performed on the mortar specimens at 7, 28 and 90 days.

3.6. Resistance Activity Index

Table 5 shows how sample M2 satisfies the minimum values (75% of the reference compressive strength). However, sample M3, which contains a 40% substitution, also has a compressive strength higher than the 60% of the reference. These strengths above the mass proportions of the cement indicate that the substitution material (VA) is also able to develop strength. This confirms the pozzolanic activity of the ashes. A hydration reaction between ash and cement is produced; therefore, it makes this material (VA) suitable for use as an active addition to cement.

Table 5. Results of Resistance activity index and resistant increase.

Designation of Mortar Specimens	Resistant Activity Index (%)			Resistant Increase (%)	
	7 Days	28 Days	90 Days	7–28 Days	28–90 Days
REF	-	-	-	26.77	20.24
M1	102.49	103.23	97.70	27.68	13.80
M2	91.33	94.00	97.78	30.48	25.08
M3	68.76	83.45	91.03	53.85	31.16

Regarding the resistance increase, it can be observed that in sample M3, which has the highest percentage of substitution, there is the greatest increase in strength at both ages. This also demonstrates the pozzolanic properties of the VA that have been studied in Section 3.3.

The sample M3 has the lowest RAI at 7 days but the highest resistant increase at 7–28 days. It is the opposite case than M1, with the highest RAI at 7 days and the lowest resistant increase at 7–28 days. This is due to the main characteristic behaviour of the pozzolanic materials, which are able to develop strength after 7 days of curing.

4. Discussion

As already mentioned above, the chemical composition of the VA agrees with a natural pozzolan, given the high values of the SiO_2 and Al_2O_3 phases, as well as the relative balance between the alkaline compounds (Na_2O y K_2O) and alkaline earth (CaO and MgO). This kind of composition favors pozzolanic reactivity between these compounds—this fact has been mentioned in the works of some researchers [34,42,43].

In contrast to what was established by Costafreda [44] in relation to the high values of loss on ignition of many pozzolans (9–13.5% for natural zeolites and 11.5–24% for bentonites), in this research, the values calculated for the LOI are not significant; this is because zeolites and bentonites are porous materials, with the ability to absorb and exchange cations, which radically differentiates them from the morphological and textural characteristics of the VA studied in this research. The origin of the VA discards the content of volatile elements since they have been expelled during the degassing process; also, there is no presence of organic matter; these aspects also explain the low LOI values. The value of the apparently high insoluble residue (IR) is caused by the fraction of SiO_2 that did not react in the solution, i.e., crystalline SiO_2 that will remain inert even during long reaction periods [44].

Regarding the quality of the VA as a pozzolan, it should be noted that almost 40% of the sample is reactive silica, values that are in concordance with the work of Rosales et al. [19]. This represents 96% of total silica, which indicates that almost all SiO_2 is available to react and develop extra strength. Another factor that allows to establish the pozzolanic nature of the VA with certainty is that, despite having high contents in total CaO, there is no presence of free CaO. This compound is totally neutralized in the test. The low free CaO contents indicate that there will be no possible expansion problems caused by its presence. Note also that the low sulphate and chloride content determined for these VAs are significantly below 0.1% and 4%, respectively, which is a determining factor in demonstrating their quality as a pozzolan [45]. A wide variety of natural pozzolans show similar behavior [46].

The results obtained in this research establish a direct correspondence between the chemical composition of the VA and its mechanical properties, as already mentioned in Section 3.1 to Section 3.3. An increase in pozzolanic reactivity occurs from shorter periods (8 days) to more advanced periods (15 days). This fact can indeed be verified with a growing increase in mechanical strength to flexion and compression from early ages (7 days) to later ages (90 days), thus establishing that the methods of analysis used in this research complement each other adequately. It is important to emphasize the fact that the pozzolanic properties of VA can be interpreted as a factor that favors not only the gain of resistances over time but also that these resistances can exceed the mechanical strength of ordinary Portland cement (OPC).

The results show how the compressive strength is higher than the reference values for low substitutions of volcanic ash. For higher additions, the compressive strength decreases. The performance in the long term is better than in the short term. However, the results are above the recommended values. Several established criteria are supported in Figure 6. It is evident that at up to 90 days of curing, there is an increase in mechanical strength; however, it is interesting to observe the individual behavior of the M-3 sample, which has the highest content of volcanic ash (OPC/VA: 60/40%). It exceeds the compressive strength recommended values (60% of the reference specimens). It supposes a more ambitious substitution than previous works [19]. At 7 days, this sample has values of initial mechanical strength significantly lower than REF; but at 28 days, that difference is visibly reduced, which is even more evident at 90 days of curing.

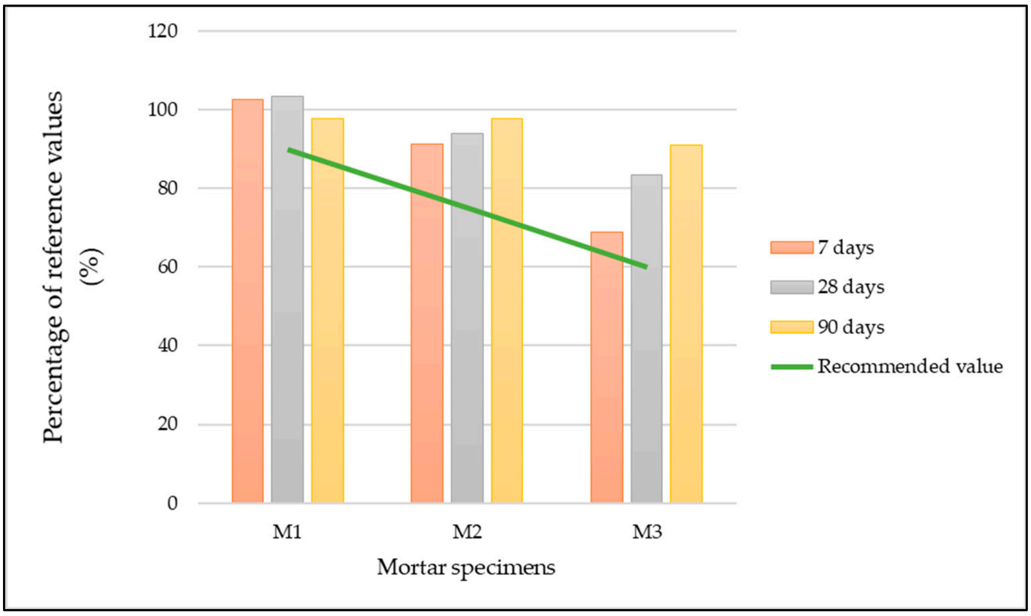

Figure 6. Comparison with recommended values.

What has been stated above is another indisputable effect of the pozzolanic activity of the VA studied in this research. From a comparative point of view with the M-1 and M-3 specimens, it is observed that M-3 has a lower mechanical behavior. Even so, its calculated resistance activity index (RAI) represents 90% of the resistance of the specimen (REF) at 90 days and 80% at 28 days of curing. The M-1 and M-2 specimens have an RAI greater than 90% of the REF value, increasing by 97% after 90 days of curing. The deductions discussed above confirm the pozzolanic activity of the volcanic ash and establish that the three projects of mixtures of Ordinary Portland Cement with volcanic ash are valid and add to the objectives of this research.

These results establish the possibility of making a significantly greater substitution concerning other materials studied [47–49] while maintaining adequate mechanical characteristics. With this, it is possible to produce a more environmentally friendly material because a significant reduction of CO_2 is achieved by eliminating up to 40% of the clinker from the cement.

In addition, it is in line with the circular economy since it should not be forgotten that this is a material derived from a volcanic eruption that, if it is not put to an appropriate use, will be treated as waste.

5. Conclusions

The results of the analyses of volcanic ash from the eruption of the Cumbre Vieja volcano on the island of La Palma lead to the following conclusions:

1. In the chemical composition by XRF and the quality chemical composition of the studied volcanic ash, a significant presence of SiO_2 y Al_2O_3 was detected, as well as alkaline compounds and alkaline earth, which permits it to be included in the group of natural pozzolan.
2. The results of pozzolanicity analysis justify the consideration of volcanic ash as a natural pozzolan. The high reactivity demonstrated by the volcanic ash with ordinary Portland cement in the solution explains the high values of mechanical strength obtained at 7, 28, and 90 days of curing.
3. The increases in mechanical compressive strengths are evidenced by an increase in the Resistance Activity Index of the M-1, M-2, and M-3 specimens above 90% in relation to the mechanical strength of the reference specimen (REF). It demonstrates that high substitutions (>25%) of volcanic ashes by cement are suitable for cements.
4. The value of the Resistance Activity Index in the M-3 at 90 days of curing is notably higher than that obtained at 7 days. It demonstrates the long-term pozzolanic activity of the ashes in terms of mechanical strength.
5. According to the mechanical behavior of the specimens studied, the formulations of OPC/VA mixtures at 10, 25, and 40% are equally effective for the production processes of pozzolanic cements, mortars, and concrete, positively affecting energy savings and reducing the emission of greenhouse gases.

Lastly, these volcanic ashes can be used in the production of cement and low-cost construction materials, making a positive social impact on the reconstruction of the urban environment affected by the eruption of the Cumbre Vieja volcano.

Author Contributions: Conceptualization: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; methodology: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; software: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; validation: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; formal analysis: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; investigation: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; resources: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; data curation: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; writing—original draft preparation: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; writing—review and editing: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; visualization: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; supervision: D.A.M. and J.L.C.; project administration: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P.; funding acquisition: L.P., S.R., C.P., D.A.M., J.L.C., B.A. and J.L.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors wish to thank the Laboratorio Oficial para Ensayos de Materiales de Construcción (LOEMCO) and the Gómez Pardo Foundation for their support of this research and publication. The authors would also like to thank the Instituto Geominero de España (IGME-CSIC) for their support in providing scientific advice.

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

References

1. González, P.J.; Tiampo, K.F.; Camacho, A.G.; Fernández, J. Shallow flank deformation at Cumbre Vieja volcano (Canary Islands): Implications on the stability of steep-sided volcano flanks at oceanic islands. *Earth Planet. Sci. Lett.* **2010**, *297*, 545–557. [CrossRef]
2. Copernicus Emergency Management Service. *[EMSR546] La Palma: Grading Product, Monitoring 22*; European Commision: Brussels, Belgium, 2021.

3. Vouffo, M.; Tiomo, I.F.; Fanmi, H.K.; Djoumen, T.K.; Ngapgue, F. Physical and mechanical characterization of pyroclastic materials in Baleng area (Bafoussam, West-Cameroon): Implication for use in civil engineering. *Case Stud. Constr. Mater.* **2022**, *16*, e00916. [CrossRef]
4. Lemougna, P.N.; Wang, K.-T.; Tang, Q.; Nzeukou, A.; Billong, N.; Melo, U.C.; Cui, X.-M. Review on the use of volcanic ashes for engineering applications. *Resour. Conserv. Recycl.* **2018**, *137*, 177–190. [CrossRef]
5. Okogbue, C.O.; Aghamelu, O.P. Performance of pyroclastic rocks from Abakaliki Metropolis (southeastern Nigeria) in road construction projects. *Bull. Eng. Geol. Environ.* **2013**, *72*, 433–446. [CrossRef]
6. Dóniz-Páez, J.; Beltrán-Yanes, E.; Becerra-Ramírez, R.; Pérez, N.; Hernández, P.; Hernández, W. Diversity of Volcanic Geoheritage in the Canary Islands, Spain. *Geosciences* **2020**, *10*, 390. [CrossRef]
7. Medina, N.F.; Barluenga, G.; Hernández-Olivares, F. Enhancement of durability of concrete composites containing natural pozzolans blended cement through the use of Polypropylene fibers. *Compos. Part B Eng.* **2014**, *61*, 214–221. [CrossRef]
8. Gomez-Arriaran, I.; Roels, S.; Abascal, I.F.; Odriozola-Maritorena, M.; Martín, K. Pore characterization of heterogeneous building materials: Pyroclastic arid–based concrete. *J. Build. Phys.* **2017**, *41*, 25–40. [CrossRef]
9. Rodríguez, E.; García, A. Lightweight Aggregate and Lightweight Concrete and its Application in the Improvement of the Thermal Properties of Volcanic Lightweight Aggregate Concrete Blocks from Canary Islands. In Proceedings of the ISRM International Workshop on Rock Mechanics and Geoengineering in Volcanic Environments, Puerto de la Cruz, Spain, 31 May–3 June 2010.
10. Lomoschitz, A.; Jiménez, J.R.; Yepes, J.; Pérez-Luzardo, J.M.; Macías-Machín, A.; Socorro, M.; Hernández, L.E.; Rodríguez, J.A.; Olalla, C. Basaltic Lapilli Used for Construction Purposes in the Canary Islands, Spain. *Environ. Eng. Geosci.* **2006**, *12*, 327–337. [CrossRef]
11. Sánchez-Fajardo, V.; Torres, M.; Moreno, A. Study of the pore structure of the lightweight concrete block with lapilli as an aggregate to predict the liquid permeability by dielectric spectroscopy. *Constr. Build. Mater.* **2014**, *53*, 225–234. [CrossRef]
12. Fajardo, V.S.; Torres, M.; Moreno, A. Hydraulic and hygrothermal properties of lightweight concrete blocks with basaltic lapilli as aggregate. *Constr. Build. Mater.* **2015**, *94*, 398–407. [CrossRef]
13. García-González, C.; Yepes, J.; Franesqui, M.A. Geomechanical characterization of volcanic aggregates for paving construction applications and correlation with the rock properties. *Transp. Geotech.* **2020**, *24*, 100383. [CrossRef]
14. Franesqui, M.A.; Yepes, J.; García-González, C.; Gallego, J. Sustainable low-temperature asphalt mixtures with marginal porous volcanic aggregates and crumb rubber modified bitumen. *J. Clean. Prod.* **2019**, *207*, 44–56. [CrossRef]
15. Franesqui, M.A.; Castelo, F.; Azevedo, M.C.; Moita, P. Construction Experiences with Volcanic Unbound Aggregates in Road Pavements. In Proceedings of the ISRM International Workshop on Rock Mechanics and Geoengineering in Volcanic Environments, Puerto de la Cruz, Spain, 31 May–1 June 2010.
16. González, P.Y.; Merino, M.D.R. Mechanical Performance of Traditional Lightweight Concretes from the Canary Islands. In *Construction and Building Research*; Springer: Berlin/Heidelberg, Germany, 2014; pp. 547–553. [CrossRef]
17. Djeunou, E.D.N.; Tsobnang, P.K.; Nkouathio, D.G.; Mohamed, R.; Giscard, D. Pozzolanic activities of some pyroclastic materials of Tombel Graben (Cameroon Volcanic Line) and potentiality for their use in construction industry. *Arab. J. Geosci.* **2021**, *14*, 1–13. [CrossRef]
18. Binici, H.; Kapur, S.; Arocena, J.; Kaplan, H. The sulphate resistance of cements containing red brick dust and ground basaltic pumice with sub-microscopic evidence of intra-pore gypsum and ettringite as strengtheners. *Cem. Concr. Compos.* **2012**, *34*, 279–287. [CrossRef]
19. Rosales, J.; Rosales, M.; Díaz-López, J.L.; Agrela, F.; Cabrera, M. Effect of Processed Volcanic Ash as Active Mineral Addition for Cement Manufacture. *Materials* **2022**, *15*, 6305. [CrossRef]
20. Fořt, J.; Černý, R. Transition to circular economy in the construction industry: Environmental aspects of waste brick recycling scenarios. *Waste Manag.* **2020**, *118*, 510–520. [CrossRef]
21. Benhelal, E.; Shamsaei, E.; Rashid, M.I. Challenges against CO2 abatement strategies in cement industry: A review. *J. Environ. Sci.* **2021**, *104*, 84–101. [CrossRef]
22. Nie, S.; Zhou, J.; Yang, F.; Lan, M.; Li, J.; Zhang, Z.; Chen, Z.; Xu, M.; Li, H.; Sanjayan, J.G. Analysis of theoretical carbon dioxide emissions from cement production: Methodology and application. *J. Clean. Prod.* **2022**, *334*, 130270. [CrossRef]
23. Data SIO, NOAA, U.S. Navy, NGA, GEBCO. Maxar Tecnologies. Google Earth. Available online: https://earth.google.com/web/@28.6439076,17.83062641,1099.82232928a,81264.90281641d,35.00003704y,-0.13362694h,0.06903636t,359.99999996r (accessed on 25 December 2022).
24. *UNE-EN-196-6:2019*; Métodos de Ensayo de Cementos. Parte 6: Determinación de la Finura. AENOR: Madrid, Spain, 2019.
25. *UNE-EN-196-7:2008*; Métodos de Ensayo de Cementos. Parte 7: Métodos de Toma y Preparación de Muestras de Cemento. AENOR: Madrid, Spain, 2008.
26. *UNE 80103:2014*; Métodos de Ensayo de Cementos. Ensayos Físicos. Determinación de la Densidad Real. AENOR: Madrid, Spain, 2013.
27. *UNE-EN 196-2:2014*; Métodos de Ensayo de Cementos. Parte 2: Análisis Químico de Cementos. AENOR: Madrid, Spain, 2014.
28. *UNE-EN 196-5:2011*; Métodos de Ensayo de Cementos. Parte 5: Ensayo de Puzolanicidad Para los Cementos Puzolánicos. AENOR: Madrid, Spain, 2011.
29. Costafreda, J.L.; Martín, D.A.; Presa, L.; Parra, J.L. Altered Volcanic Tuffs from Los Frailes Caldera. A Study of Their Pozzolanic Properties. *Molecules* **2021**, *26*, 5348. [CrossRef]

30. *UNE-EN-196-1:2018*; Métodos de Ensayo de Cementos. Parte 1: Determinación de Resistencias. AENOR: Madrid, Spain, 2018.
31. Al-Fadala, S.; Chakkamalayath, J.; Al-Bahar, S.; Al-Aibani, A.; Ahmed, S. Significance of performance based specifications in the qualification and characterization of blended cement using volcanic ash. *Constr. Build. Mater.* **2017**, *144*, 532–540. [CrossRef]
32. Hossain, K.M. Blended cement using volcanic ash and pumice. *Cem. Concr. Res.* **2003**, *33*, 1601–1605. [CrossRef]
33. Olawuyi, B.J.; Olusola, K.O. Compressive Strength of Volcanic Ash/Ordinary Portland Cement Laterized Concrete. *Civ. Eng. Dimens.* **2013**, *12*, 23–28.
34. Ndjock, B.D.L.; Elimbi, A.; Cyr, M. Rational utilization of volcanic ashes based on factors affecting their alkaline activation. *J. Non-Cryst. Solids* **2017**, *463*, 31–39. [CrossRef]
35. Tchakoute, H.; Elimbi, A.; Yanne, E.; Djangang, C. Utilization of volcanic ashes for the production of geopolymers cured at ambient temperature. *Cem. Concr. Compos.* **2013**, *38*, 75–81. [CrossRef]
36. Bondar, D.; Lynsdale, C.; Milestone, N.; Hassani, N.; Ramezanianpour, A. Effect of heat treatment on reactivity-strength of alkali-activated natural pozzolans. *Constr. Build. Mater.* **2011**, *25*, 4065–4071. [CrossRef]
37. Ghafoori, N.; Najimi, M.; Radke, B. Natural Pozzolan-based geopolymers for sustainable construction. *Environ. Earth Sci.* **2016**, *75*, 1110. [CrossRef]
38. Siddique, R. Properties of concrete made with volcanic ash. *Resour. Conserv. Recycl.* **2012**, *66*, 40–44. [CrossRef]
39. Siddique, R. Effect of volcanic ash on the properties of cement paste and mortar. *Resour. Conserv. Recycl.* **2011**, *56*, 66–70. [CrossRef]
40. Alraddadi, S.; Assaedi, H. Characterization and potential applications of different powder volcanic ash. *J. King Saud Univ.-Sci.* **2020**, *32*, 2969–2975. [CrossRef]
41. Játiva, A.; Ruales, E.; Etxeberria, M. Volcanic Ash as a Sustainable Binder Material: An Extensive Review. *Materials* **2021**, *14*, 1302. [CrossRef]
42. Presa, L.; Costafreda, J.L.; Martín, D.A.; Díaz, I. Natural Mordenite from Spain as Pozzolana. *Molecules* **2020**, *25*, 1220. [CrossRef]
43. Costafreda, J.; Martín, D. Bentonites in Southern Spain. Characterization and Applications. *Crystals* **2021**, *11*, 706. [CrossRef]
44. Costafreda, J.L. Geología, Caracterización y Aplicaciones de las Rocas Zeolitizadas del Complejo Volcánico de Cabo de Gata, Almería. Ph.D. Thesis, Universidad Politécnica de Madrid, Madrid, Spain, 2008; 515p.
45. *UNE-EN 197-1:2011*; Cemento. Parte 1: Composición, Especificaciones y Criterios de Conformidad de los Cementos Comunes. AENOR: Madrid, Spain, 2011.
46. Santana, J.J.; Rodríguez-Brito, N.; Blanco-Peñalver, C.; Mena, V.F.; Souto, R.M. Durability of Reinforced Concrete with Additions of Natural Pozzolans of Volcanic Origin. *Materials* **2022**, *15*, 8352. [CrossRef]
47. Chen, X.; Chen, H.; Chen, Q.; Lawi, A.; Chen, J. Effect of partial substitution of cement with Dolomite powder on Glass-Fiber-Reinforced mortar. *Constr. Build. Mater.* **2022**, *344*, 128201. [CrossRef]
48. Li, Q.; Qiao, H.; Li, A.; Li, G. Performance of waste glass powder as a pozzolanic material in blended cement mortar. *Constr. Build. Mater.* **2022**, *324*, 126531. [CrossRef]
49. Xiao, H.; Zhang, F.; Liu, R.; Zhang, R.; Liu, Z.; Liu, H. Effects of pozzolanic and non-pozzolanic nanomaterials on cement-based materials. *Constr. Build. Mater.* **2019**, *213*, 1–9. [CrossRef]